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APPROACHES FOR IN-PLANT REDUCTION OF SPENT PULPING LIQUOR LOSSES

SPECIAL REPORT NO. 12-02

MAY 2012

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PRESIDENT'S NOTE

Effective management of organic material generated in chemical pulp manufacturing processes is important for optimizing mill operations, as well as for meeting effluent quality objectives. While the recovery and regeneration of spent pulping chemicals is a central component of virtually all chemical pulping facilities, there are ongoing routine losses of these chemicals due to the complex nature of the processing systems, and these are either recovered back into the process or are sent to wastewater treatment systems. Reducing and recovering losses of spent pulping liquors can result in better performance of wastewater treatment systems, decreased "pass through" of substances that may resist biological degradation, and incremental benefits to the mill's energy generation and chemical cost profiles.

In contrast to "spills" of spent pulping liquor, "losses" occur on a relatively ongoing basis, given that daily facility operations result in both intentional and unintentional releases of dilute spent liquor into the process sewer system. These losses do not typically lead to a regulatory exceedance, but can contribute to effluent characteristics such as colour and foam. In the context of Canada's Environmental Effects Monitoring (EEM) regulation, these relatively low-level losses may be significant relative to EEM field monitoring results, depending on site-specific circumstances. In these instances, a better understanding of current research into the interconnections between managing spent pulping liquor and enhanced effluent management, along with identifying practical tools to assess the strengths and weaknesses of a facility's systems for reducing and managing these low-level background losses may be extremely useful.

This report has been designed as a tool that provides a proposed framework that may be useful to individual facilities in helping to identify and minimize "background" low-concentration and/or low-flow spent liquor losses, thus reducing the challenges inherent in managing wastewater treatment systems and effluent quality. This approach may also be useful for facilities currently working to address residual effects measured through the EEM program or to address local receiving environment initiatives, depending on site-specific circumstances.

Ronald A. Yeske

May 2012

NOTE DU PRÉSIDENT

Gérer efficacement les matières organiques qui se forment dans les procédés de fabrication de la pâte chimique est important lorsqu'il s'agit d'optimiser les activités d'exploitation d'une usine et d'atteindre les objectifs de qualité de l'effluent. Bien que la récupération et la reconstitution des produits chimiques dans la liqueur usée soient des composantes cruciales dans l'exploitation de pratiquement toutes les usines de pâte chimique, il y a constamment des pertes de ces produits chimiques en raison de la nature complexe des systèmes de traitement. Ces pertes sont soit récupérées et retournées dans le procédé, soit acheminées vers le système de traitement des eaux usées. En réduisant et en récupérant ces pertes, on peut améliorer la performance du système de traitement des eaux usées, diminuer la quantité des substances qui sont résistantes à la biodégradation et qui sont rejetées avec l'effluent final et réaliser des gains supplémentaires en matière de production d'énergie et de coûts des produits chimiques.

Contrairement aux « déversements » de liqueur usée, les pertes surviennent assez régulièrement. En effet, les activités quotidiennes de l'usine engendrent des rejets accidentels et intentionnels de liqueur usée diluée dans le réseau d'égout du procédé. Ces pertes n'entraînent généralement pas un dépassement de norme, mais peuvent modifier les caractéristiques de l'effluent (p. ex. un changement de couleur et la présence de mousse). Cependant, selon les conditions d'exploitation des usines, ces pertes de liqueur usée, dont la concentration ou le débit est relativement faible, peuvent devenir significatives lorsqu'elles sont mesurées sur le terrain dans le cadre du règlement canadien sur les études de suivi des effets sur l'environnement (ESEE). Dans ces situations, il pourrait s'avérer extrêmement utile d'approfondir les travaux de recherche sur les liens qui existent entre la gestion de la liqueur usée et une meilleure gestion de l'effluent et d'identifier des outils pratiques pour évaluer les forces et les faiblesses des systèmes d'une usine qui servent à réduire et à gérer ces pertes.

Le présent rapport propose un cadre de travail qui pourrait s'avérer utile aux usines qui cherchent un moyen de localiser et de réduire ces pertes et ainsi atténuer les difficultés liées à la gestion des systèmes de traitement des eaux usées et à la gestion de la qualité de l'effluent. Cette approche peut aussi être utile aux usines qui cherchent présentement des solutions dans le cadre du programme des ESEE pour éliminer les effets résiduels ou qui réalisent des projets locaux dans le milieu récepteur.

Ronald A. Yeske

Mai 2012

APPROACHES FOR IN-PLANT REDUCTION OF SPENT PULPING LIQUOR LOSSES

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ABSTRACT

Effective management of losses of organic material derived from pulp manufacturing is an important aspect of environmental management at chemical pulp mills. While the recovery of pulping chemicals is a central component of virtually all chemical pulping facilities, there are ongoing routine losses of these chemicals due to the nature of the processing systems, and these are either recovered back into the process or are sent to wastewater treatment. Reducing and recovering losses of spent pulping liquors can result in better performance of wastewater treatment systems, decreased "pass through" of substances that may resist biological degradation, and incremental benefits to the mill's energy generation and chemical cost profiles. This report has been designed as a tool to provide a proposed framework that may be useful to individual facilities in helping to identify and minimize "background" low-concentration and/or low-flow spent liquor losses, thus reducing the challenges inherent in managing wastewater treatment and effluent quality. This approach may also be useful for facilities currently working to address residual effects measured through the EEM program or to address local receiving environment initiatives, depending on site-specific circumstances. The report includes example mill programs for managing spent liquor losses.

KEYWORDS

best management practices, biological response, EEM, receiving water effects, spill control, spent liquor

RELATED NCASI PUBLICATIONS

Technical Bulletin No. 919 (August 2006). *Review of color control technologies and their applicability to modern kraft pulp mill wastewater.*

Technical Bulletin No. 860 (May 2003). *Pulp Mill Process Closure: A Review of Global Technology Developments and Mill Experiences in the 1990s.*

Technical Bulletin No. 805 (May 2000). *Examination of Alternative Statistical Methods for Monitoring BMP Performance*.

Technical Bulletin No. 378 (August 1982). *Effluent foam control practices*.

Technical Bulletin No. 276 (August 1974). *Spill Prevention and Control Aspects of Paper Industry Wastewater Management Programs*.

APPROCHES DE RÉDUCTION DES PERTES DE LIQUEUR USÉE EN USINE

RAPPORT SPÉCIAL N^{O} 12-02
MAI 2012

RÉSUMÉ

Gérer efficacement les pertes de matières organiques provenant de la fabrication de la pâte chimique est un élément important dans la gestion des usines de pâte chimique sur le plan de l'environnement. Bien que la récupération des produits chimiques dans la liqueur usée soit une composante cruciale dans l'exploitation de pratiquement toutes les usines de pâte chimique, il y a constamment des pertes de ces produits chimiques en raison de la nature des systèmes de traitement. Ces pertes sont soit récupérées et retournées dans le procédé, soit acheminées vers le système de traitement des eaux usées. En réduisant et en récupérant ces pertes, on peut améliorer la performance du système de traitement des eaux usées, diminuer la quantité des substances qui sont résistantes à la biodégradation et qui sont rejetées avec l'effluent final et réaliser des gains supplémentaires en matière de production d'énergie et de coûts des produits chimiques. Le présent rapport propose un cadre de travail qui pourrait s'avérer utile aux usines qui cherchent un moyen de localiser et de réduire ces pertes et ainsi atténuer les difficultés liées à la gestion des systèmes de traitement des eaux usées et à la gestion de la qualité de l'effluent. Cette approche peut aussi être utile aux usines qui cherchent présentement des solutions dans le cadre du programme des ESEE pour éliminer les effets résiduels ou qui réalisent des projets locaux dans le milieu récepteur. Le rapport fournit des exemples de programmes mis sur pied par certaines usines pour gérer les pertes de liqueur usée.

MOTS-CLÉS

effets sur le cours d'eau récepteur, ESEE, liqueur usée, meilleures pratiques de gestion, mesures de contrôle des déversements, réponse biologique

AUTRES PUBLICATIONS DE NCASI

Bulletin technique n° 919 (août 2006). *Review of color control technologies and their applicability to modern kraft pulp mill wastewater.*

Bulletin technique n° 860 (mai 2003). *Pulp Mill Process Closure: A Review of Global Technology Developments and Mill Experiences in the 1990s*.

Bulletin technique n° 805 (mai 2000). *Examination of Alternative Statistical Methods for Monitoring BMP Performance*.

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APPROACHES FOR IN-PLANT REDUCTION OF SPENT PULPING LIQUOR LOSSES

1.0 INTRODUCTION

Consistently meeting effluent quality objectives involves effective management of losses of organic material to sewer and successful use of wastewater treatment systems. While the recovery of pulping chemicals is a central component of virtually all[1] chemical pulping facilities, there are ongoing routine losses of these chemicals, due to the complex nature of the processing systems, which are either recovered back into the process or are sent to wastewater treatment. These losses, which are different from larger "spills", can occur within the pulp processing and pulping chemical recovery systems, from pumps, valves, knotters, screens, washers, and other equipment, as well as through intentional diversions from the evaporators (e.g., during boil-outs), digesters (e.g., during hard or soft cooks), and during start-up and shutdown operations. Losses can also occur unintentionally through human error, tank overfilling, or mechanical failure. Reducing and recovering losses of spent pulping liquors can result in better performance of wastewater treatment systems, decreased "pass through" of substances that may resist biological degradation, and incremental benefits to the mill's energy generation and chemical cost profiles (NCASI 1982, 2006; Amendola ,Vice, and McCubbin 1996; USEPA 1997).

This document provides perspective on designing and implementing best management practices for reducing in-plant spent pulping liquor losses, along with a summary of potential benefits. Routine, systemic, or inadvertent "losses" of relatively low concentration spent pulping liquor are the focus of this report, rather than sudden larger volume of higher concentration "spills". Information is provided on the chemical characteristics of spent pulping liquors, approaches for evaluating the effectiveness of liquor loss control provisions, and example spent liquor loss management plans from four bleached kraft mills. An overview of wastewater treatment system and effluent management benefits is provided, along with a discussion of results from field studies examining in-stream patterns in Canada's Environmental Effects Monitoring (EEM) Program and biological response patterns associated with mill upgrades.

2.0 ORIGIN AND NATURE OF SPENT PULPING LIQUOR

In a kraft pulp mill, spent pulping liquor refers to the organic-rich liquor produced in the digester by the reactions of white liquor, a solution of sodium hydroxide and sodium sulphide, with wood chips under high temperature and pressure. These reactions preferentially dissolve the lignin component of the wood relative to the carbohydrate portion, though some cellulose and hemicelluloses are dissolved as well. A typical yield of pulp from a digester in a mill that manufactures bleached kraft market pulp is on the order of 45% of the amount of dry wood processed. Thus, about one half of the wood material is dissolved into the digester liquor and becomes part of the spent pulping liquor.

Kraft digesters may be of either batch or continuous type. In batch processing, multiple units are used to maintain a continuous flow of pulp, as time is required to fill, heat, cook and empty each unit. At the end of each batch cook, the digester contents are released under pressure into a blow tank. The processing of both the pulp and the spent pulping liquor becomes continuous from this point forward.

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[1] While all kraft pulping facilities recover their spent pulping liquor, there are constraints facing sulphite pulping mills that do not use magnesium as a pulping base. Very few non-magnesium base sulphite mills are in operation today.

Continuous digesters mix the white liquor with the wood chips at one end and they flow co-currently through the unit. In some digesters, extraction screens pull spent liquor from unit partway through the vessel. At the downstream end of the digester, the contents are typically pumped to the blow tank for further processing.

From the blow tank, the pulp/liquor mixture is processed to remove the partially cooked wood pieces, known as knots. Knotters are screening devices used to effect the removal of the knots. Some spent pulping liquor may be discharged with the rejected knots, and this can be a liquor loss point. Knots may be returned to the digester or disposed of and the entrained spent liquor may be recovered or discharged, respectively.

The mixture then flows to an operation known as brown stock washing, in which fibres are separated from the dissolved components that comprise spent pulping liquor. The objective in brown stock washing is to produce a pulp which contains an acceptable amount of entrained spent pulping liquor using as little water as possible. This is accomplished using one or more pulp washing units arranged in series so that the washing liquid flow is counter-current to the direction of the pulp flow. There are several different types of devices used for this purpose, but they all have in common some type of screen mesh or drilled plate that retains the pulp while allowing the wash liquor to pass through. A typical brown stock washing system will have many tanks, pumps, valves and other devices that represent points of potential spent liquor losses. The spent liquor ranges in concentration from 0.5% or less at the pulp discharge end of the washing process to on the order of 12% to 20% at the initial washing stage.

Before, during, or after brown stock washing the pulp is screened to remove fibre bundles, and other particulate contaminants from the stock. Older technology involves use of so-called “open” screening performed at ambient pressure. Due to the tendency of these units to generate foam, dilution water is typically added. The pulp is then dewatered and the excess water discharged to sewer, producing a significant loss of spent liquor. Due to the large volume and very dilute nature of this liquor, recovery is prohibitively expensive. Modern pulp screening systems utilize pressurized devices that generate little or no liquid discharge to sewer.

Spent pulping liquor from the filtrate tank of the first brown stock washing stage, known as weak black liquor, contains from 12 to 20 % dry solids by weight. These solids include the spent pulping chemicals as well as the organic matter dissolved from the wood. The spent liquor is processed to recover and reconstitute the pulping chemicals and to extract the chemical energy contained in the organic matter. The weak liquor is first concentrated in multiple-effect evaporators to about 50% dry solids. This “strong” liquor is further concentrated to 65% or more solids using direct or indirect contact evaporators and fired in a chemical recovery furnace in which the organic matter is combusted and the inorganic chemicals recovered. Mills with direct contact evaporators may practice oxidation of black liquor to lower the potential for reduced sulphur gas emissions from the recovery furnace. There are a number of opportunities in the various evaporation and oxidation processes for spent liquor to escape into area sewers.

Black liquor storage tanks are used extensively to provide for operational flexibility. These tanks and the piping and pumps that transfer spent liquor to and from them are also potential loss points.

Spent pulping liquor from a kraft mill is composed of inorganic and organic constituents. The inorganic component derives mainly from the white liquor used to cook the wood and includes sodium as the predominant cation and hydroxide, sulphide, carbonate, sulphate, thiosulphate and chloride as the major anions. Table 2.1 shows the elemental composition range of virgin black liquors from North American wood species.

Table 2.1 Elemental Composition of Kraft Black Liquor Solids from North American Wood Species (Adams et al. 1997)

Element	% by weight
Carbon	34 – 39
Hydrogen	3 – 5
Oxygen	33 – 38
Sodium	17 – 25
Sulphur	3 – 7
Potassium	0.1 – 2
Chloride	0.2 – 2
Nitrogen	0.04 – 0.2
Other	0.1 – 0.3

Organic compounds comprise the majority of the black liquor solids. Most of the individual compounds are unknown, but they are generally classified according to the wood constituents from which they were derived. The largest organic component is alkali lignin, consisting of mostly large condensed, cross-linked macromolecules containing many aromatic groups including phenols, catechols and quinones (Grace and Malcolm 1989). The carbohydrate wood components are present in the spent liquor as hydroxy acids and carboxylic acids. Extractives are the third major group of organic compounds. They consist of resin acids, fatty acids, and neutrals (e.g., sterols and terpene alcohols), and generally pass through the pulping process unchanged. Table 2.2 shows typical concentration ranges of organic compound groups for spent kraft liquors.

Table 2.2 Chemical Species in Kraft Black Liquor (wt. % of dry solids) (Adams et al. 1997)

Compound	% wt of dry solids
Alkali lignin	30 – 45
Hydroxy acids	25 – 35
Extractives	3 – 5
Acetic acid	5
Formic acid	3
Methanol	1
Sulphur	3 – 5
Sodium	15 – 20

Many of the organic constituents are biodegradable and therefore represent an oxygen demand during biological wastewater treatment. Estimates of the BOD_5 of spent pulping liquors are difficult to find owing to the challenge involved in measuring the BOD_5 of this material. NCASI recently conducted some analyses to estimate the BOD_5 and COD of several black liquors. On average, the BOD_5 concentration was about 0.12 kg/kg black liquor solids (BLS), and the COD about 1.0 kg/kg BLS.

2.1 Causes of Spent Liquor Losses

There are many causes of spent liquor losses in a pulp mill. In general, they are the result of a combination of limitations in process design, control systems, and equipment capacities, and/or weaknesses within operating procedures or maintenance practices. Some typical causes include

- routine evaporator boilouts;
- brownstock washing process control problems;
- contamination of condensates due to overloaded or poorly maintained evaporators;
- liquor system imbalances;
- leaking pump packings;
- insufficient evaporation capacity;
- sub-optimal planning around scheduled maintenance shutdowns and start-ups;
- insufficient maintenance of spent liquor processing equipment;
- gaps or weaknesses in standard operating procedures (SOPs) and operator training; and
- inadequate provisions (e.g., sumps, pumps and tanks) to recover spent liquor that escapes the process.

2.2 Department-Level Contribution of Organic Material to Wastewater Treatment Loading at Kraft Mills

For bleached kraft mills, the largest source of organic material[2] to the wastewater treatment (WWT) system typically originates from the bleach plant. Bleach plant effluents derived from softwood pulping normally have larger COD loads than effluents derived from hardwood pulping, and alkaline sewers typically have larger COD loading than acidic sewers. Any process that limits organic material to the bleach plant, such as oxygen delignification or increased bleach plant filtrate recycle, tends to limit the amount of organic material discharged to the WWT. Yousefian and Reeve reported department-level COD contributions from four bleach kraft pulp mills in the United States and Canada, in which sufficient data for one mill were presented to ascertain relative COD mass loading contributions from various mill areas (Yousefian and Reeve 2000). Their results showed that, of the effluents analyzed, the recovery area effluent had the highest COD concentration, and the bleach plant effluent had the largest COD loading to the WWT (Table 23). It is presumed that the “recovery area” effluent embodies intermittent liquor spills from the recovery area. Arsenault and Brezniak (1997) presented COD mass loading amounts for a mill producing primarily bleach kraft paper and market pulp from softwood and hardwood furnish). Their results showed that the largest COD mass loading contributor to the waste water treatment plant was the bleach plant effluent (Table 2.4). The “kraft mill” sewer includes black liquor from spills and process upsets. At unbleached kraft pulp mills, COD loading from the pulping and recovery area potentially becomes a much larger contributor to the overall COD loading to the wastewater treatment system. If the bleach plant COD loading contribution is removed for the two cases in Table 23 and 2.4 and other loading values remain the same, the COD loading contribution from kraft pulping and recovery becomes 18% and 32%, respectively, of the measured COD loading amounts to the WWT.

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[2] Measured as COD.

High molecular weight (HMW) material from kraft mill effluents can be classified as either hydrolyzable (chemically broken down with water) or non-hydrolyzable (resistant to chemical reaction with water). Hydrolyzable HMW material in kraft effluents consist primarily of carbohydrates; non-hydrolyzable HMW material consist primarily of oxidized lignin. Strömberg et al. (1996) presented results of effluent treatment plant removal of HMW material from seven bleach kraft pulp mills, pulping softwood and hardwoods, with various bleaching technologies and effluent treatments systems. On average, the removal percentage of the non-hydrolyzable HMW material was 8%, while the removal percentage of the hydrolyzable HMW material was 80%. Yousefian and Reeve (2000) showed that the non-hydrolyzable HMW material had the lowest treatability of the effluent fractions studied (average treatability of 34% from four mills), signifying that the non-hydrolyzable HMW material was most resistant to conventional effluent treatment. The authors showed that the non-hydrolyzable HMW fraction in sewers associated with the brown side of the mill (i.e., kraft recovery, digester, wood room, brown stock, etc.) was greater than in sewers associated with other parts of the mill (i.e., bleach plant, paper machine area, etc.). Non-hydrolyzable HMW material comprised 45% of the organic material in sewers associated with the brown side of the mill versus 22% of the organic material associated with other sewers in the mill (Yousefian and Reeve 2000). These studies indicate that non-hydrolyzable HMW material may be found in relatively high concentrations in sewers associated with the brown side of the kraft mill, and that the treatment efficiencies of this material can be expected to be lower than other types of organic material found in kraft mill sewers.

Table 2.3 Bleach Kraft Mill COD Mass Balance from Yousefian and Reeve (2000)

Sewer	COD (kg/admt)	COD (% contribution to untreated effluent)
Stock Preparation	2	7
Acidic Bleach Plant	3.5	13
Alkaline Bleach Plant	13	46
Paper Machine Area	5	18
Recovery Area	1.5	5
Sum of Sewers	25	89
Untreated Effluent	28	

Table 2.4 Bleach Kraft Mill COD Mass Balance from Arsenault and Brezniak (1997)

Sewer	COD (% contribution to untreated effluent)
Kraft Mill[a]	11
Condensates[b]	4
Bleach Plant[c]	25
Coated Paper Machine[d]	14
Uncoated Paper Machine[e]	5
Sum of Sewers	59
COD Mass Loading Not Accounted For	41

[a] Includes seal water, screen rejects, pressure knotter rejects when knot recovery is not operating, fibre and black liquor from spill and process upsets, process cooling waters, and sand separators.
[b] Includes foul condensates from the NCG system, evaporator foul condensates, and foul condensates from the kraft mill blow heat accumulator, secondary condensers, and relief condensers as well as combined condensates.
[c] Includes acidic and alkaline bleach plant effluent, and sodium sesquisulfate overflow from the salt cake slurry tank in the chlorine dioxide generation plant.
[d] Includes paper machine white water, Uhle box effluent, fibre from the fourth stage cleaning system, fillers from the colour screen backwash, cooling water from the oil coolers, process losses from the colour kitchen, and paper machine additives such as dyes, sizing and starches.
[e] Includes paper machine whitewater, fibre, fillers, cooling water, and Uhle box effluent.

3.0 IN-PLANT SPENT LIQUOR LOSS REDUCTION

Individual facilities inherently have unique operational and functional limitations in the extent to which the organic material in process streams and sewers can be recovered, and therefore a systematic process engineering-driven approach to reviewing in-plant processes can be effective in assessing a site’s opportunities and constraints in managing these losses. Irrespective of whether a specific organic compound within in-plant process streams may be targeted for reduction, or whether reduction of overall organic losses is sought, application of a systematic approach to reviewing in-plant processes has been found to lead to identification of lower capital cost, effective opportunities to manage and reduce these losses rather than focusing only on optimizing wastewater treatment (Amendola, Vice, and McCubbin 1996; USEPA 1997; Vice and Stuart 2000). This type of systematic in-plant approach may also be effective as a tool in addressing “investigation of cause” and “investigation of solutions” requirements for compliance with Canada’s Environmental Effects Monitoring (EEM) regulation.

3.1 Scope of Spent Liquor Loss Reduction Approach

Inadvertent losses to sewer of organic material (e.g., wood fibre) occur with all types of pulping processes, and are associated with virtually all process streams carrying fibre, water, and process chemicals. In chemical pulping mills, this organic material is accompanied by inorganic spent pulping chemicals that have an inherent energy and chemical value. In mechanical pulping mills, residual organic material in process streams is essentially accompanied only with water. Thus, the use of chemical recovery systems at chemical pulping mills provides a ready-made opportunity for recovery of spent liquor losses, whereas mechanical pulping, given its relative lack of use of chemicals[3], is not inherently designed for organic loss recovery. To that effect, in this report, only chemical pulping process spent liquor loss reduction will be discussed. The approaches reviewed can be applied to kraft, sulphite, and semi-chemical pulping operations, for which the in-plant reduction of organics loss is better known as in-plant reduction of "spent pulping liquor", as it will be referred to from here forward.

3.2 Liquor Loss Reduction Philosophy

By law, all pulp and paper facilities in Canada are required to report and respond to spills that may lead to an exceedance of their regulatory requirements. However, daily operations result in both intentional and unintentional losses of dilute spent liquor into the process sewer system that may not lead to a regulatory exceedance. These background losses are not considered to be spills and are not managed in the same way.

In designing its approach to the effluent guidelines in the United States, the U.S. Environmental Protection Agency (USEPA) specifically identified losses of spent liquor-related materials as having a potential ongoing, rather than sudden or acute, effect on wastewater treatment, and thus, potentially, on the receiving environment (USEPA 1997). As such, USEPA's best management practices (BMPs) for spent liquor losses are largely oriented towards managing systemic *losses of spent liquor* rather than spills, though the actions involved also help contain and manage larger spills.

Distinguishing daily management of spent liquor losses from emergency handling of spills is of significant importance for the mill to achieve benefits from implementing spent liquor management strategies. Undertaking a systematic analysis of potential spent liquor loss points associated with regular mill operations, rather than focusing on potential sources of rare spill events, is the pivotal difference between developing a liquor loss management program that will act to minimize potential receiving environment concerns related to daily mill effluent discharges versus a spill management program that allows continued background-level liquor losses to enter wastewater treatment while only focusing on infrequent significant liquor loss events. Following site-specific implementation of engineering analyses and BMP plans in the US, these mills have achieved more consistent and reliable biological treatment, reduced potential for release of substances that resist biological degradation, and enhanced recovery and reuse of pulping chemicals. (See Section 11 and Amendola, Vice, and McCubbin 1996.)

For these reasons, the focus of this report is on *effective management of systemic losses of spent pulping liquor*. The report does not consider approaches for handling of rare spill events, which are discussed in a previous NCASI Technical Bulletin (NCASI 1974).

3.3 Site-Specific Context

Spent liquor loss management is an inherently site-specific endeavour. While there are components of a liquor loss management program that may be common to a number of facilities, each mill site has its own unique process unit configuration and sewer system, and this drives the nature and practicality of approaches that can be designed to mitigate spent liquor losses. In addition, each facility's unique staff plays a key role in optimizing a liquor loss control program.

The engineering approach discussed in this report inherently allows for "bottom-up" liquor loss management approaches, quite literally starting with a review of the mill's underground sewer system (U-drains). Review of a mill site's process operations in relation to its physical layout and existing

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[3] With the exception of chemi-thermomechanical pulping.

structures will increase the likelihood that a facility will arrive at the most practical and cost-effective program for its unique situation. In addressing liquor loss management within its efforts to meet USEPA's effluent guidelines, mills have specifically identified flexibility as being an inherent component of an effective program; thus, facilities in the US have implemented a wide array of approaches to manage and reduce losses of spent pulping liquor. Several case studies illustrating these approaches are discussed in Section 11 of this report.

4.0 DEFINITIONS

In the remainder of this report, a number of phrases will be used to describe aspects of the design and implementation of an in-plant systematic review of pulping, washing, and liquor recovery processes. These terms are described more completely here, for reference.

Spent pulping liquor - For kraft and soda mills, spent pulping liquor means black liquor that is used, generated, stored, or processed in the pulping and chemical recovery processes. For sulphite mills, spent pulping liquor means any intermediate, final, or used chemical solution that is used, generated, stored, or processed in the sulphite pulping and chemical recovery processes (e.g., ammonium-, calcium-, magnesium-, or sodium-based sulphite liquors).

Spill event – An unpredictable, acute discharge of spent pulping liquor from pulping or chemical recovery systems, resulting from equipment failure or operating error, which has significant potential to adversely impact wastewater treatment plant operations and effluent quality.

Liquor loss – The routine discharge of spent pulping liquor from pulping or chemical recovery systems due to limitations in process designs, control systems, equipment capacities, operating procedures or maintenance practices.

Immediate process area - The location at the mill where pulping, screening, knotting, pulp washing, pulping liquor concentration, pulping liquor processing, and chemical recovery facilities are located; generally, the battery limits of the aforementioned processes. Immediate process area includes spent pulping liquor storage and spill control tanks located at the mill, whether or not they are located in the immediate process area.

Recovery of spent pulping liquor – Spent pulping liquor is normally captured and processed in a chemical recovery process that is integrated with the chemical pulping process, in order to regenerate the pulping chemicals and extract the energy associated with the wood-derived organic matter.

Intentional diversion – The planned removal of spent pulping liquor, soap, or turpentine from equipment items in spent pulping liquor, soap, or turpentine service by the mill for any purpose including, but not limited to, maintenance, grade changes, or process shutdowns.

Turpentine and soap[4] - Turpentine refers to kraft sulphate turpentine which is a mixture of terpenes, principally alpha- and beta-pinene, recovered primarily from the condensation of digester relief gases from the cooking of softwoods by the kraft process. Soap refers to tall oil soap, which is the product of reaction between the alkali in kraft pulping liquor and fatty and resin acids of the wood, which precipitate out of the liquor during evaporation.

[4] Note: In Canada, almost none of either of these is purposely separated and sold, though there may be some degree of this. Usually it is either kept in solution, or separated and then burned as fuel. There is typically too little of it inadvertently produced by wood species pulped in Canada to render it a profitable co-product.

Engineering analysis – A systematic technical analysis of the process equipment, tankage, and systems in spent pulping liquor service, to determine the magnitude and routing of spent liquor leaks, spills, and intentional diversions under a variety of operating conditions, such as normal operations, start-ups and shutdowns, maintenance outages, weather-related events, power failures, and grade changes. An engineering analysis may identify capital projects that can enhance the performance of a BMP program.

5.0 ENGINEERING FOUNDATION FOR SPENT LIQUOR LOSS CONTROL

A thorough review of a mill's process equipment, sewer system, and wastewater treatment system can be used as the basis for a systematic engineering analysis to identify the most cost-effective approaches for reducing low-level losses of spent pulping liquor (Vice and Stuart 2000).

The components described in the following sections may be helpful in undertaking a logical, step-by-step approach to a liquor loss engineering analysis that will result in a series of site-specific best management practices (BMPs) for spent liquor loss control. The information presented in these sections of the report reflects the direct field and work experience of the authors, along with personal communication the authors have had over the past 20 years with well over three dozen facilities across North America and Europe, and is consistent with the approaches published to date in the literature (Amendola, Vice, and McCubbin 1996; USEPA 1997; Vice and Stuart 2000). The results of this type of systematic analysis can ultimately become the foundation for a BMP program for reducing planned and unplanned losses of spent pulping liquor to the mill's sewer system.

5.1 Put Together a BMP Engineering Analysis Team

Given that effective liquor loss management requires the knowledge and cooperation of engineers, supervisors, and operators from multiple departments, a team approach where the team is made up of people who have complimentary backgrounds can be ideally suited to undertake an engineering analysis related to spent pulping liquor BMPs. The combination of engineers with solid operational backgrounds in the fibreline and recovery areas, along with engineers who understand the wastewater treatment system, and pulping/recovery area operators who have worked at the mill for many years can help generate specific, yet realistic, ideas that staff across the mill will feel comfortable buying into. Given the spectrum of expertise brought to the table, such a team will be able to identify activities within the operation that potentially contribute to low-level losses of spent pulping liquor, including loss points that have not been documented in mill process diagrams and/or which have not traditionally been seen as potentially contributing to environmental releases. In contrast with the reliance on only mill environment staff for the development of traditional approaches to improve the quality of final mill effluent, effective spent pulping liquor BMPs tend to be accomplished through harnessing the experience and knowledge of fibreline and recovery area process engineering and operations staff (Vice and Stuart 2000).

To enable this team to achieve its maximum effect, support from the top of the facility's management can help tremendously, in that this support conveys to the entire mill that the engineering analysis and BMP program will become part of the facility's ongoing environmental objectives, rather than a one-time analysis to identify areas where spent pulping liquor losses could be improved.

5.2 Set Battery Limits for BMPs

Before beginning the engineering analysis, the extent of the area within the facility that will be reviewed and which will subsequently be the focus of spent pulping liquor BMPs needs to be defined. Three areas of the mill are related to spent pulping liquor loss reduction, and thus generally become the battery limits for BMP development.

- Fibreline: from the point at which water is added to the chips through to the point at which the pulp enters the bleach plant, including all related sewers and sumps
- Recovery Area: from the point at which spent pulping liquor from the fibreline area is sent to the recovery area through to the entrance of the liquor to the recovery boiler, including all related sewers and sumps
- Wastewater Treatment: from the points at which sewer collection points or sumps merge together to enter primary treatment through to the discharge from the secondary biological treatment system

These three areas can be explicitly defined through specific process unit operations and their related entry and exit points, and are most easily identified by denoting them on the mill drawings used during the analysis. The battery limits essentially become the framework within which solids and water balances will be developed, and they become the basis for carving out sub-areas that will be reviewed in detail with operators and maintenance staff through a series of personal interviews, to identify intentional and unintentional loss points from the process. Pairing process and instrumentation diagrams with sewer diagrams can be extremely helpful, so that during the analysis, the ultimate fate of any liquor losses from the processing units can be physically correlated with specific sewer lines.

5.3 Develop Steady-State Material Balances Around and Inside Battery Limits

Once the battery limits are defined, steady-state material balances can be developed for spent black liquor solids (BLS) and process flows, using available flow, pulp consistency, and percent BLS information. While mills do not typically have sufficient available information to undertake a highly precise balance, there is frequently enough information to enable the construction of a sufficiently accurate picture of the distribution of flows of BLS and water throughout the pulping, recovery, and wastewater treatment areas for the purposes of the BMP engineering analysis.

For the purposes of an engineering analysis, an Excel-based mass balance is, at most, what is needed. The utility of the balances quickly becomes self-evident, as usually there are areas of the process that have potential loss points with particularly high solids content, and this can aid in targeting priority areas for the engineering analysis that will lead to the most successful results. Also, areas within the analysis where the balance does not adequately close are indicative of process areas or sub-areas where more analysis and/or information gathering will be needed—or indeed, where some of the inadvertent loss points may be located. Process simulation programs can be used for more extensive investigations into spill system design (Lundström et al. 2003).

Balances may need to be generated for different operating configurations, for example, if different wood furnishes are run on the same line, under different operating conditions.

The balances are typically optimized when accompanied with interviews of mill operators and maintenance staff, given that they have explicit knowledge regarding typical steady-state and non-steady-state spent liquor exit points, which can help close the balance for a given process unit. Some of these spent liquor exit points may be surprising to the team undertaking the engineering analysis, given that mill staff are usually trained to be highly focused on maintaining process operation stability, and thus may be unaware that certain exit points used for operability reasons may carry a relatively high concentration of solids relevant to a spent liquor management strategy. Harnessing this hands-on knowledge and integrating it within the engineering analysis may be one of the most significant aspects in identifying lower-cost opportunities for spent liquor loss BMPs.

To confirm the accuracy of the balance, particularly where estimates have been made regarding liquor loss points, quick, small-scale sampling can confirm the relative concentration of spent liquor solids [along with some contextual information such as pH, conductivity, and organics (e.g., COD), if desired]. This sampling can help the BMP team confirm areas of the pulping and recovery areas that contribute more spent liquor losses to sewer and could thus be targets for action within the facility's BMP program.

5.4 Understand the Mill's Current Liquor Loss Management Philosophy

In order to analyze the mill's potential opportunities in terms of managing spent pulping liquor losses, it is useful to understand the mill's current approach, whether explicit or implicit, for minimizing losses of liquor. Each mill's systems and procedures for dealing with these types of losses aggregate into what might be called a philosophy behind their approach (Vice and Stuart 2000)—an overarching characterization of the manner in which mill equipment and staff work together to minimize liquor losses to the environment. Examples of liquor loss management philosophies can include minimizing capital expenditure associated with managing liquor losses, seeking to address losses at their point of occurrence, addressing losses immediately before their release, etc. It may be that different areas of a facility use quite different philosophical approaches and these may be more or less tied to minimizing environmental releases versus ensuring optimal process conditions. Having different philosophies in different areas of the mill may make sense for many reasons; the value to the BMP engineering analysis is that understanding the current philosophy will typically lead to an effective identification of opportunities for reducing background spent liquor losses.

The degree to which capital equipment versus operator intervention through standard operating procedures (SOPs) manages liquor losses can fundamentally alter the nature and extent of effective management approaches in place, and thus determine the availability of low-cost options for reducing background losses to the sewer. Mill experience to date has shown that more than any other factor, engagement of operators and other mill staff has the most significant positive influence in identifying straightforward opportunities for mitigating inadvertent and planned losses of liquor to sewer (Vice and Stuart 2000). While the existence of capital equipment may provide capacity for containment and recovery of certain types of losses, there is significant value from harnessing the perspective offered by operators who intimately understand the nature of the equipment for which they are responsible, including the points at which the operation may release losses to sewer. Facilities that have effective BMPs in place have found that capital equipment may simply allow a liquor loss to be carried across shifts, rather than fostering its management directly at its point of origin (Amendola, Vice, and McCubbin 1996).

The choices made by a facility in terms of relying on capital equipment versus operating practices are evidence of the facility's liquor loss management philosophy. The degree to which there are further opportunities to enhance standard operating procedures or whether capital equipment investments would be needed ultimately affects whether further action on liquor loss control will be more or less cost-effective for a given facility.

5.5 Review Process Areas and Undertake Interviews with Operating Staff

While the initial definition of BMP battery limits and development of solids and water balances will have provided the BMP team with a reasonable understanding of the scope of developing the facility's BMP program, an on-the-ground review of key process areas complements this initial scoping exercise. Identifying the main process flows in relation to their areas of containment, drainage areas, sumps, U-drains, and sewer destinations helps place a physical, three-dimensional frame on top of the process. Understanding things such as the layout of the pulping and recovery areas, the locations of equipment and tankage, as well as understanding battery limits for operator control and maintenance staff are key to designing a BMP program that is practicable for the mill in question. The following is a list of some aspects for the BMP team to consider while reviewing the pulping, recovery, and wastewater treatment areas of the mill.

- What is the physical layout of relevant process equipment, as well as the location and naming conventions for liquor tanks?
- What are the main process flows as identified on a process flow diagram, and where are they physically located in relation to drainage patterns, containment areas, sumps, and sewer configurations?
- What and where (process-wise, and physically) are the planned and unplanned liquor loss points during typical modes of operation (start-up, shutdown, maintenance, production grade or rate changes, power failure, storm events, and normal operation)?
- What are the percent spent liquor solids and flow rates of liquor loss points?
- How reliable are the various units of process equipment, and what are their individual histories?
- What are the sources and relative amounts of fresh water mixing with spent liquor in U-drains?
- What is the type and capacity for liquor loss diversion, containment, and recovery?
- What fibre recovery and separation systems are currently being used?
- What instrumentation is used to monitor and detect losses of spent pulping liquor, and what actions are taken above which thresholds?
- Where do tank and equipment overflows go?
- What is the condition of the U-drains, and how frequently are they used?
- What are the roles of staff responsible for specific areas of the process, including transition points from one process to another (in terms of design, operation, and maintenance)?
- How are plant inspections and walk-throughs conducted, by whom, how frequently, and how are they documented?
- How do the main equipment controls work, and what do they respond to?
- What are the process bottlenecks (in the context of spent pulping liquor), and what are the key challenges to managing them?
- How are temporary operating conditions communicated across mill staff?
- How are shift changes managed, in the context of spent pulping liquor inventories?
- How are inter-departmental issues (between pulping and recovery, between recovery and wastewater treatment, etc.) managed?
- How are liquor loading, unloading, and transfers of material accomplished?
- How are storm water and other accumulations drained from diked areas?

In conjunction with the on-the-ground process area review, an increased understanding of the mill's current process liquor losses, and the management strategy for dealing with them, can be accomplished by carrying out through a series of personal interviews with all engineers, operators, and maintenance staff operating in each of the three areas of the mill being reviewed for the engineering analysis. During these interviews, the capital equipment (e.g., sumps, tanks) and SOPs that are in place for each specific area (fibreline, recovery, and wastewater treatment) can be identified, for achieving the following functions for both intentional and unintentional liquor losses:

- avoiding losses altogether;
- controlling losses to minimize their volume where they do occur;
- containing and recovering losses back to process (including methods to separate high solids streams from less concentrated streams); and
- containing and metering losses to wastewater treatment.

Undertaking the interviews is not so as to judge whether the current actions and/or equipment are adequate; it is essentially to make an inventory of the tools the facility currently has in its toolbox. These current tools ultimately influence the degree of flexibility available to make lower-cost operational changes (versus more costly capital equipment changes) to reduce liquor losses, and can help identify approaches in one area of the mill that may also work effectively in another area.

The interviews can serve to review in detail how each area of the mill operates during procedures such as

- normal operations;
- start-up and shutdown;
- power failure;
- production grade or rate changes;
- maintenance; and
- storm and weather events.

In particular, the potential magnitude and routing of liquor losses (both systemic losses and those due to specific operating scenarios) can be estimated.

This interviewing point in the engineering analysis can be an extraordinarily useful contributor to the ultimate effectiveness of the BMP strategy that will arise as a consequence. One approach to consider is asking the operators to draw the processes they manage on a white board, identifying all spent liquor loss points. As development of this drawing is undertaken, the use of "what if" questions and inquiries about infrequent events that would demand operator attention can help the engineering analysis team identify previously unknown operating circumstances. Also, given that the environmental nature of specific process unit operations is not necessarily readily apparent, once the operator understands what is meant by "background losses of spent liquor," a number of previously unknown liquor loss points will begin to appear on the white board process flow diagram. Such perspective is extremely valuable when undertaking a spent liquor BMP engineering analysis, and this interview strategy can coincidentally result in significant buy-in from the operators, as they learn more about their direct roles in meeting the mill's spent liquor loss BMP objectives.

Additional aspects that can be derived from the interviews include perspective on whether the current spent liquor loss management philosophy is creating any challenges with the process operations. For a facility with relatively few existing approaches for minimizing liquor losses from the system, containing and recovering these losses can be an operational challenge. Understanding the specific operating conditions that create the greatest liquor loss challenges can be helpful to the engineering analysis team when they are designing recommended approaches for liquor loss management.

The interviews can be used to identify

- detailed information on relevant process operations;
- the site's spent liquor loss history (both internally tracked and losses triggering spill reporting requirements), incorporating information from interviews with operators as well as written logs;
- estimated liquor losses that would be considered steady background losses (intentional or unintentional);
- estimated liquor losses that would be considered intermittent based on operating conditions (intentional);
- potential for unintentional spent liquor losses from each unit within the pulping, washing, and recovery areas of the mill;
- potential order of magnitude of liquor losses (from pump gland/packing leaks, to split lines, to tank overflows, to complete line or tank failure); and
- ability of existing capital equipment to contain and recover spent liquor losses.

5.6 Establish Inventory of Relevant Capital Equipment

An inventory of current capital equipment relevant to spent liquor loss management can help identify the extent to which current equipment and monitoring may be sufficient and where gaps may exist. The most effective spent liquor loss management programs tend to rely less on capital equipment and more on the role of operators and maintenance staff as well as low capital cost refinements in process design (Amendola, Vice, and McCubbin 1996). That said, it is unlikely that effective implementation of a spent liquor BMP program can be undertaken without some level of capital expenditure (USEPA 1997).

An inventory of relevant equipment can be very broad, including process vessels, seal tanks, condensate and liquor tanks, sumps, sewers, dikes, curbing, and paving. The inventory can also include characteristics for each listed item such as volume, monitoring and process controls (e.g., automatic, connection with DCS, etc.), physical containment (or ultimate fate of release) and/or equipment design that mitigates losses from the area (e.g., seal water separation).

5.7 Prepare Sewer Configuration and Wastewater Treatment Diagrams

The connection between the processing areas and the wastewater treatment system is physically manifested in the mill's underground sewer system (U-drains). While process lines are designed to carry specific materials related to the fibreline and recovery area, the sewer system carries losses external to the process lines themselves, and may carry spent liquor-related materials on a frequent or infrequent basis. Historically, many mills have an underground sewer system directly connected to the wastewater treatment entry point, frequently with an option for bypass to a holding tank or pond for diversion of wastewater if substantial losses (i.e., spills) occur (NCASI 1974). As noted above, these types of significant losses are rare, and thus, the underground sewer system may become an unintended vehicle for lower concentration spent pulping liquor losses and/or may carry essentially clean water that could render the collection of other downstream liquor loss sources economically impracticable, simply through dilution. Understanding the configuration of the mill U-drain and sewer system is therefore a critical component of the engineering analysis.

The underground sewer system is ideally depicted using a flowsheet that illustrates sumps, pumps (identifying back-ups), pump capacities, instruments, set points, data collected to a distributed control system, drainage information (specific overflows), and the collection and recovery systems for drainage systems, if they exist. The interconnection of the underground sewer system with the process itself (fibreline and recovery areas) and the mill wastewater collection and treatment system is also useful to depict.

Finally, the mill's wastewater treatment system itself, including any associated spill holding areas and/or recovery systems can be a helpful tool in completing the picture of all equipment related to spent liquor loss generation, collection, recovery, and treatment.

5.8 Collate Spill History and Potential for Liquor Loss

While spent pulping liquor BMPs focus on background losses of liquor, and not spills, exploring the mill's record of historic spills (reportable and non-reportable) can provide important information during the engineering analysis, to help target priority weaknesses in the fibre and liquor management systems. For this reason, it can be helpful to verify both on-site and public records to consider how and why these spill events happened. As this internal review is undertaken, the engineering analysis team can discuss whether some were related to ongoing and/or intermittent inadvertent or advertent losses, while identifying aspects that may be incorporated into spent pulping liquor BMPs.

Information related to historic spill events can be most easily reviewed in tabular form, by area, identifying all historic and potentially significant liquor loss events (e.g., tank failure/overflow, instrument failure, etc.). Information regarding flow, time, concentration assumption, likelihood of future recurrence, and potential fate for such a loss event can also be valuable.

5.9 Practicable Recovery Analysis

For a mill to determine the extent to which spent pulping liquor losses can be practicably and cost-effectively recovered back into the process (versus collection and wastewater treatment), three analyses are useful (Amendola, Vice, and McCubbin 1996; Vice and Stuart 2000):

- economic analysis of liquor loss recovery;
- quantification of recovery system capacity; and
- stress analysis of wastewater treatment system.

5.9.1 *Economic Liquor Loss Recovery Analysis*

The economic component of the practicable recovery analysis involves an estimation of the concentration of spent pulping liquor above which it may be economic for the mill to recover, and below which it is not economic to recover. The two components to the analysis—cost and benefit—are weighed against each other. The chemical and energy value of the recovered material (benefit) is compared with the estimated costs for evaporating and causticizing that material, with an offset of avoided wastewater treatment.

To render such a screening-level economic analysis practical, it is necessary to make several assumptions regarding liquor loss recovery. For example, it must be assumed that the incremental recovery of the additional liquor does not limit mill production; that the additional recovered liquor is recovered directly to the evaporators and not via pulp washing; and that there is no capital cost recovery for liquor loss recovery equipment.

Components of the economic liquor loss recovery analysis that contribute *cost* include

- evaporator steam used for increasing the solids concentration of incremental recovered liquor, x (unknown, and expressed as % BLS), up to the solids concentration of mill weak black liquor (y %, known for a given facility);
- evaporator steam used for increasing the concentration of incremental weak black liquor up to the concentration of heavy black liquor;
- chemical make-up for lime kiln; and
- disposal (i.e., recovery) of lime mud.

Components of the economic liquor loss recovery analysis that contribute *benefit* include

- fuel value of incremental recovered pulping liquor;
- chemical value of recovered sodium; and
- cost avoidance for wastewater treatment.

The break-even point is the concentration x % BLS at which the *cost* equals the *benefit*. This concentration is only relevant in terms of normal operations such as start-up, shutdown, etc. There may be different operational, cost, and volume constraints on the lowest concentration at which additional spent liquor can be recovered. While some facilities that are under extremely tight effluent permit requirements may recover down to roughly 1% liquor solids (Amendola, Vice, and McCubbin 1996), it is more typical to recover down to the range of 3 to 4% (USEPA 1997).

The equation for this calculation is provided below (modified from Vice and Stuart 2000).

$$Cost = V_L + V_{RC} + V_{WWT} - C_{EL} - C_{EW} - C_L$$

Where:

Cost = incremental cost to recover additional spent pulping liquor ($/kg BLS).

V_L = liquor fuel credits, related to the incremental credit ($/kg BLS) for reduced need for fuel due to the additional recovered liquor burned in the recovery boiler.

V_{RC} = recovered chemical credits, related to the incremental credit ($/kg BLS) due to reduced need for make-up chemicals.

V_{WWT} = treatment credit, related to the incremental credit ($/kg BLS) from not having to treat the additional BOD associated with the additional recovered liquor.

C_{EL} = evaporator steam cost for recovered liquor, related to the incremental cost ($/kg BLS) to evaporate additional recovered liquor up to known y %, from its initial unknown concentration of x %.

C_{EW} = evaporator steam cost for known *y* % liquor, related to the incremental cost ($/kg BLS) to evaporate the additional weak (*y* %) liquor to the concentration entering the recovery boiler.

C_L = lime make-up and mud disposal cost ($/kg BLS), related to the incremental cost for lime and recovery of lime mud for the additional recovered liquor.

The value for C_{EL} incorporates the unknown solids concentration (*x* %) for the additionally recovered spent pulping liquor. Resolving the equation for the economic recovery breakeven point (i.e., where *Cost* = $0) allows derivation of the concentration of spent pulping liquor above which it may be economic for the mill to recover and below which it would not be economic to recover.

5.9.2 *Quantification of Recovery System Capacity*

The degree to which additional increments of spent pulping liquor can be recovered within a mill's current configuration largely depends on the existing liquor retention time within the fibreline and recovery area. Incremental spent pulping liquor recovery can be significantly enhanced if there is an accompanying approach to increase the concentration of the material being recovered (e.g., diverting clean streams from spent liquor loss collection points), given that it is rare that small additional amounts of spent liquor solids will constrain the recovery boiler and more likely that constraints quickly arise in tank volume availability and evaporator capacity (McCubbin 1996). The extent to which enhanced recovery of spent liquor losses is estimated to add to recovery system load is typically within the anticipated range of most mills' available recovery area capacity and, arguably, within the range of accuracy of measurement of the recovery system load, itself.

5.9.3 *Wastewater Treatment Stress Analysis*

An important component in developing a cost-effective spent liquor management plan is an understanding of the mill's wastewater treatment plant's (WWTP) capacity to treat spent liquor losses without causing effluent quality excursions or potential effects on the receiving environment. The primary impact of spent liquor on biological treatment systems is the additional BOD_5 load exerted by components of the dissolved organic matter. Biological treatment systems are typically designed to ensure adequate removal of BOD_5 over a range of anticipated loading conditions and temperatures, establishing the size of the components such as the biological reactors, secondary clarifiers (if present) and the number, size, and arrangement of aeration/mixing devices. Thus, the design basis is a good starting point for understanding the capacity of a biological treatment system. However, some treatment systems are operated beyond their original design basis due to mill reconfiguration or production increases, and so would be expected to have less capacity to absorb a spent liquor spill than their design basis might indicate. Thus, the objective of the stress analysis is to determine the largest spent liquor spill that will not degrade effluent quality beyond permitted levels, given the current system capability. This could be accomplished by reviewing and evaluating historical operating data and/or by conducting simulations using a computer-based predictive model that has capability to accommodate dynamic loading inputs. Calibration of the model over a range of loading conditions, especially high loading conditions, is essential to obtaining credible predictions. Worst-case conditions are typically during coldest temperatures, during which biological metabolism and therefore rate of treatment are at a minimum.

5.10 Generate Practical Recommendations for BMPs

Once the interviews have been undertaken and the practicable recovery analysis has provided an indication of the degree to which further spent liquor loss may be possible, the engineering analysis team can brainstorm to generate a list of strengths and weaknesses related to each area of the mill that is under review, according to a hierarchy of the most efficient, cost-effective approaches to reduce spent liquor losses:

- opportunities to avoid losses by identifying locations where the likelihood of spent liquor loss can be reduced;
- areas where new or improved standard operating procedures (SOPs) could reduce the risk or magnitude of potential liquor loss;
- areas where enhanced monitoring would provide operators with additional useful information to control or limit potential losses of spent pulping liquor;
- opportunities within the process where spent liquor losses could be directly recovered back into related process equipment;
- opportunities within the process where spent liquor losses could be economically collected and metered back into process equipment;
- opportunities to re-route cleaner water to enable concentration of spent pulping liquor losses to enable recovery; and
- locations where there would be no opportunity for liquor loss recovery, and routing to wastewater treatment (e.g., via a spill basin) would be the only remaining option.

Various aspects of the spent pulping liquor system and/or its operation can be modified with little to no capital cost to enhance existing recovery system capacity. For example, developing standard operating practices to keep spent liquor tank inventories as low as practicable can provide spare capacity for use during maintenance activities. There is no one right or wrong way to minimize low-concentration losses of spent pulping liquor; each facility has its own operational and economic challenges, and opportunities to reduce these losses.

There may be cases where it is not possible to readily identify the relative concentration of a given intermittent or continuous loss point of spent pulping liquor. In these cases, it may be useful to conduct a small sampling initiative (e.g., three days during average operating conditions) to characterize specific streams for parameters such as conductivity, pH, TSS, and organic content (e.g., COD, BOD, TOC, etc.).

The team can initially identify proposed changes to work practices (e.g., SOPs or operational modifications) or opportunities for undertaking relatively low-capital cost initiatives (e.g., re-routing clean water within a U-drain), as well as areas where more extensive capital equipment may be needed. This can be undertaken on a process area-specific basis to aid in developing a plan for enhancing current approaches for liquor loss control. In addition, the team can identify appropriate in-process monitoring approaches that will enhance the utility of any physical or operational changes that may be made. In many cases, simply having compiled these opportunities into one document or tabular format can lead to a more comprehensive, systematic approach for considering options for reducing liquor losses. Interestingly, some of the most effective liquor loss management systems have been employed at older mills with limited spill tank capacity, where site personnel have been empowered to develop and apply work practices that leverage the unique capabilities of the site's equipment (Amendola, Vice, and McCubbin 1996).

6.0 THE ROLE OF WORK PRACTICES AND SITE PERSONNEL

One of the most significant contributors to effective control of spent pulping liquor losses is the role of trained site personnel (Amendola, Vice, and McCubbin 1996; USEPA 1997; Vice and Stuart 2000). Involving operators and maintenance staff in the development of a mill site's liquor loss control philosophy and in the evolution of a mill's BMP program is the single most effective approach that can be taken, in terms of maximizing opportunities for relatively low-cost approaches to avoid and recover losses of spent pulping liquor prior to wastewater treatment.

Operators and maintenance staff may be unfamiliar with the environmental aspects related to the processing equipment in their care, given that their daily objectives are largely related to maintaining and operating the system in such a way that the process throughput is optimized and there is minimal downtime. Indeed, while the operators are aware that at times there may be low-level losses of spent pulping liquor to sewer, it may be that they unfamiliar with the nature of these losses in terms of their potential effect on wastewater treatment. In terms of maintenance staff, they may be unaware that liquor losses to sewer occurring at different concentration levels may have different types of effects on wastewater treatment, and that relatively minor maintenance issues can contribute more significantly to spent liquor losses than they may imagine. Simply raising awareness of the specific connections between the operating areas of the mill and the opportunities to decrease low-level spent liquor losses to sewer may lead to useful ideas for reducing these releases from process operations.

6.1 Work Practices

Work practices, or SOPs, are the most efficient way to approach liquor loss minimization, as they are the least costly methods for reducing these losses and among the quickest to implement. Given that a BMP program is focused on low-concentration losses of spent pulping liquor and not on larger spills, SOPs can be designed to minimize liquor losses to sewer at source or to aid in their segregation by concentration level, which in turn could increase potential for their efficient recovery. In practice, BMP-related SOPs tend to be a combination of existing work practices, where liquor loss management is newly incorporated, and new work practices to manage opportunities identified by the BMP team during the engineering analysis.

A foundation for optimizing BMP-related work practices can be to seek approaches that help with the ongoing, daily management of spent pulping liquor inventories. This objective typically becomes most challenging during shift changes and at facilities that have grown accustomed to having larger storage “pockets” in the process where spent pulping liquor can accumulate for periods of time. It is much more difficult and time-consuming to recover backlogged spent pulping liquor storage than to employ approaches that foster continual management of that inventory across the process. Indeed, the more optimized the liquor inventory management, the less reliant operators are on emergency storage capacity, and thus, the lower the potential capital costs for implementing a BMP program.

Another work practice that can significantly contribute to ongoing reduction of spent pulping liquor losses is seeking approaches that increase the frequency of operator walk-throughs in the pulping and recovery process areas. In cases where operators are able to act on minor issues immediately (e.g., tightening pump packings), this enhances the utility of these frequent walk-throughs, as they can result in timely, active contributions to minimizing unintentional losses of liquor.

6.2 Preventive Maintenance

Preventive maintenance is a core component of a successful BMP program. During its development of a spent liquor loss BMP regulation, USEPA undertook a synthesis of pulp and paper mill spill information reported to their Emergency Response Notification System between 1988 and 1993, and identified mechanical failure as the cause of nearly half (45%) of the reported spills (USEPA 1997). Other causes included human error (20%), tank overfilling (16%), intentional diversions (4%), and unknown (13%). While the location and nature of intermittent and/or systemic low-level spent liquor losses can be dramatically different from spent liquor spills, the causal factors are interrelated, and this data set suggests that preventive maintenance may be a way to limit losses due to mechanical failure.

All mills have site-wide maintenance programs in response to the continual need to address the impacts of daily production on the mill’s process equipment. That said, the BMP team may identify opportunities to place specific effort on areas and/or equipment that may be more likely sources of higher concentration spent liquor losses. In addition, in some cases, it may be possible to use enhanced preventive maintenance to offset the need for capital equipment.

Preventive maintenance also includes inspection and repair procedures, the combination of which allows for the design of a proactive, rather than reactive, approach to minimizing unintentional losses of spent pulping liquor.

6.3 Leak Detection

As part of the mill’s preventive maintenance program, a combination of tank visual inspection and integrity testing can provide a platform for directing maintenance and/or capital investment that could decrease the potential for a catastrophic spent liquor loss event. In addition, to the extent that low-level spent liquor losses could occur from liquor tanks, such a leak detection program is a useful complement to other low or non-capital-intensive BMP program elements.

6.4 Integrating BMPs into Site Modification Planning

Spent liquor loss BMP programs are grounded in the physical connections between units of process equipment, process liquor pipelines, underground drainage systems, and the wastewater treatment facility. Therefore, physical modification to any of these aspects of the facility would lead to a need to revisit the site’s BMP program, to consider any related modifications that may need to be undertaken. Modifications that involve rerouting of drains and/or process lines can alter the configuration and/or extent of a sump’s collection area, and may alter the degree to which that sump’s contents can be recovered back into the pulping or spent liquor recovery systems.

6.5 Training

Given that mill staff play such a prominent role in designing and implementing an effective BMP program, staff training is a key aspect to maximizing spent liquor loss control. Once the BMP program is in place, periodic training, usually in conjunction with broader environmental training initiatives, can help in identifying opportunities to improve BMPs and to consider areas where the program is not working as well as it might. The operators and maintenance staff are the most likely to be focused on areas where the BMP can be reshaped to foster the most efficient approaches to reducing spent liquor losses, given that ideally these practices could be woven into their daily procedures in a manner that would not deflect them from achieving their process objectives.

To help mill staff focus on reducing relevant sources of pulping liquor losses, it may help if they focus on the notion that a loss of spent pulping liquor is not a spill. While staff may be extremely familiar with the regulatory and site-specific requirements related to a sudden spill of material, it is less likely they would typically consider an ongoing low-level loss of spent pulping liquor to be of concern, given that these losses may be part of daily operations and are ultimately treated in the wastewater treatment plant. Therefore, building this notion into BMP training can help staff clarify the objectives of the facility’s BMP program.

7.0 THE ROLE OF CAPITAL EQUIPMENT

An engineering analysis is likely to identify opportunities to improve a mill's spent liquor loss management program that would involve new or modified infrastructure, equipment, or controls. However, a spent liquor BMP plan does not have to include significant capital expenditures (e.g., replacing process equipment), even in older mills that lack modern pulping washing, screening, and recovery systems. In general, capital investment can be minimized by implementing a BMP program that focuses on 1) harnessing mill operations and maintenance staff to integrate BMPs into mill operations; 2) diverting clean streams from potential liquor loss areas to avoid dilution of recovered spent pulping liquor; 3) collecting diverted spent liquor at the highest possible liquor solids concentration; 4) returning collected liquor and fibre to the process at optimal locations; 5) isolating (with curbs and dikes) critical process areas from the WWTP; and 6) using conductivity monitoring in strategic areas to alert operators of loss events. In particular, diverting very low concentration or clean streams to sewer is extremely important in minimizing additional loading potential on spent liquor evaporators (NCASI 2003).

Examples of capital improvements include

- curbing and dikes to direct losses to a sump where they can be recovered;
- secondary containment for spent liquor tanks;
- sewer sumps and pumps;
- piping to route recovered losses to an appropriate point in the process;
- segregation of pump seal water;
- spent liquor tank overflow alarms; and
- monitoring, alarm and control systems.

In some cases, major capital investment might be warranted if the engineering analysis determines that the primary causes of spent liquor losses are related to issues inherent in the design of the fibreline and/or recovery process operations, and there is environmental compliance-driven impetus to addressing losses. Some examples of this type of more significant investment include replacing an open pulp screening system with modern closed screening, and retrofitting or replacing evaporators to increase capacity. That said, undertaking more significant capital expenditures typically requires co-benefits (e.g., production increases, environmental compliance-related outcomes) to render such an option feasible.

8.0 DEDICATED MONITORING AND ALARM SYSTEMS

Effective spent liquor loss management depends on knowing when losses are occurring and taking action, either manually or automatically, to stop the loss and/or initiate material recovery. Monitors are typically used on spent liquor tanks to indicate impending or existing overflow conditions, and these are used to alert operators that some action needs to be taken. Within process areas, the use of monitors in floor drains or sumps is commonly practiced to indicate the need for some action by the operator, or to trigger such action automatically. Conductivity monitors are used for this purpose as they tend be very robust sensors with a long history of use in the industry. Other types of monitors, including pH, temperature, and colour may also find application in process area monitoring.

Beyond the immediate process areas, many mills monitor their major sewers and/or combined mill wastewater prior to treatment as a means of identifying significant loss events that require investigation or corrective action and to track the performance of the overall BMP program. Most US mills that are required to implement spent liquor BMPs conduct such monitoring via lab analysis of 24-hour composite samples. Several different parameters are in common use for this purpose, including chemical oxygen demand (COD), colour, and total organic carbon (TOC). Where these analyses are employed, it may be advantageous to remove suspended solids prior to conducting the test, as this will remove fibres and other solids which may not be good indicators of spent liquor losses. It should also be noted that there is no test parameter that is entirely specific to spent liquor. All of these parameters will also respond to changes in bleach plant operations that might affect the quality of sewered filtrates. COD would also respond to losses of white liquor, green liquor, and weak wash due to their reduced sulphide content. Colour measures optical properties of the wastewater and is therefore subject to biases resulting from metal ions (iron and manganese), sulphide, and perhaps other materials.

Data collected from influent wastewater monitoring can be used to track performance of the mill's overall BMP program. Quality control charts are used for such purposes and a variety of statistical measures can form the basis of such charts. A general approach to implementing control charts is to conduct monitoring over some period (US mills were required to conduct monitoring for six months initially) and use the data to develop control limits that would trigger certain actions such as investigation of causes or corrective actions. Data should be screened to remove outliers and checked for normality and independence prior to calculating control limits. Such data are not usually independent, but rather the individual data points are autocorrelated to data points close in time to one another. The effect of this is that the average is not constant, but rather exhibits a trend. Statistical techniques are available to correct for autocorrelation and these can be incorporated into control charts (NCASI 2000).

US mills regulated under the Cluster Rule spent liquor BMPs are required to establish both a lower and upper action level based on statistical analysis of six months of operating data. If measured values exceed the lower action level for a period of time specified by the mill, an investigation is triggered to determine the cause of the excursion. If the upper action level is exceeded for the designated period of time, mills are required to carry out some corrective action to bring the monitoring parameter back into control. The lower action level, typically set at the mean plus two standard deviations, is analogous to an upper warning limit on a process control chart. The upper action level, typically set at the mean plus three standard deviations, is analogous to an upper control limit. Action levels may be established based on other statistical measures, but in any case should be based on careful analysis of the data to minimize false alarms on the one hand, and maximize the detection of significant events on the other.

9.0 ESTIMATED COST

During the development of USEPA's spent liquor BMP regulation, cost estimates were developed for implementing BMPs in mills in three categories, based on the extent to which a facility already has related capital equipment and spent liquor loss prevention systems in place (USEPA 1997, p. 9-1).

Category 1: Mills with most of the major components of a model spent pulping liquor control system in place. Incremental investment costs at these mills are not expected to exceed 10% of the estimated total investment cost (for a mill with no such system in place).

Category 2: Mills with some of the major components of a model spent pulping liquor system in place (e.g., a few liquor collection sumps, liquor storage tanks, sewer conductivity monitoring, etc.). At these mills, as much as 60% of the estimated total investment costs may be necessary to fully implement a BMP Plan.

Category 3: Mills with relatively little spent pulping liquor control equipment in place. At these mills, as much as 90% of the estimated total investment costs may be required to implement a BMP Plan.

In 1996, the US industry was estimated to have roughly half of its chemical pulping mills in Category 3, with between a quarter and a third in the other two categories. This range would have been typical for the industry in both the US and Canada, at that time. The estimated total costs for implementing a BMP program included

- between five and nine liquor collection sumps (depending on mill complexity);
- liquor storage capacity (one 500,000 gallon tank);
- one to two fibre reclaim tanks (depending on mill complexity);
- process area curbing and diking;
- turpentine and soap containment (for softwood kraft mills);
- conductivity monitoring and tank level alarms; and
- the cost for undertaking a BMP engineering analysis and BMP plan development.

The related capital investment costs to implement an entire BMP program in 1996 were estimated to range from roughly \$3.1 million in 2012 dollars (for a single-line kraft mill) to \$5.8 million in 2012 dollars (for a complex kraft mill). Additional annual costs (for evaporation of recovered liquor, operation and maintenance of new equipment, tank integrity testing, and operator training) and operating benefits (due to recovered fibre, recovered pulping chemicals, recovered energy, and reduced wastewater treatment costs for power, nutrient addition, and sludge disposal) were also identified, but were not estimated. From responses to USEPA's questionnaire, facilities indicated net savings of between \$0.20 and \$1.00 per ton of brownstock pulp, after implementation of a BMP program similar to that characterized above (USEPA 1997).

10.0 POTENTIAL ENVIRONMENTAL BENEFITS FROM REDUCTION OF IN-PLANT LOSSES OF ORGANICS

Reducing and recovering losses of spent pulping liquors can result in better performance of wastewater treatment systems and decreased pass-through of substances that may resist biological degradation. Each is discussed below.

10.1 Enhanced Performance of Wastewater Treatment Systems

Minimizing and/or recovering losses of spent pulping liquor can reduce the load to a mill's wastewater treatment system and reduce the variability in untreated wastewater load, thus leading to more stable treatment system performance. In turn, this more stable performance of the wastewater treatment system can result in less variability in effluent performance criteria.

While foaming of mill wastewater within a mill's wastewater treatment system can have certain beneficial properties (e.g., retaining heat within an aerated stabilization basin during colder months of the year), it is generally considered to be at best a nuisance, and at worst a safety hazard for effective maintenance of wastewater treatment system equipment (NCASI 1982, 1966). Foam is caused by substances that are surface active, which lower the surface tension of a solution, leading to foaming when the solution is aerated (e.g., during wastewater treatment). The presence of spent pulping liquor in mill wastewater can lead to foaming, with more dilute liquor causing higher degrees of foaming than stronger spent liquor (NCASI 1982). To the degree that spent pulping liquor can be minimized in mill wastewater, there is a concurrent benefit in reducing foaming potential during wastewater treatment.

A subset of mills in North America has final effluent permit constraints for colour (NCASI 2007). While in theory a somewhat subjective concept, colour can be quantitatively measured using specific techniques for application to pulp and paper mill effluents (NCASI 2011). Numerous factors can affect the generation (or indeed, reversion) of colour in a mill's effluent, including wood species, reduction in pre-bleach plant Kappa number (e.g., through oxygen delignification), and spent pulping liquor losses (NCASI 2006). For facilities under such constraint, there may be benefits in terms of effluent colour reduction that can result from reduced losses of spent pulping liquor to wastewater treatment, particularly since a BMP program can be a less capital cost-intensive approach to reducing losses of lignin or spent pulping liquor in comparison to implementing oxygen delignification or extended cooking.

10.2 Decreased Release of Substances That May Resist Biological Degradation

Pulp and paper mill effluent is among the most studied of industrial effluents. This is due, in part, to the environmental effects of oxygen demand, solids, and nutrient and organic loading in receiving waters prior to routine effluent treatment (Owens 1991), and to the large volumes discharged into surface waters relative to most other industrial effluents. Environmental effects prior to effluent treatment included habitat degradation due to reduced oxygen concentration in the water column [owing to high biochemical oxygen demand (BOD) loading], habitat degradation from deposition of solids and fibre, and acute toxicity (Owens 1996). With regulation and industry efforts to curtail these effects, the research focus shifted to identifying and eliminating the chemical(s) thought to be responsible for acute biological toxicity including resin and fatty acids (Pacheco and Santos 1999), chlorinated phenolics (Owens 1991), persistent chlorinated organic compounds (Servos et al. 1994), and the reduction and elimination of the use of elemental chlorine in bleaching.

As process modifications and effluent treatment improved effluent quality (e.g., Kovacs et al. 2003; Martel, Kovacs, and Berubé 2009), the concerns over acute toxicity and habitat degradation decreased, and the focus shifted to the potential for effluent exposure to cause more subtle, sublethal effects such as reduced growth or reproduction. Fish are the primary organism in these studies, but because effects at other trophic levels are integrated into higher level responses, some field studies have incorporated other trophic levels such as macroinvertebrates and algae. The largest and most notable of these are Canada's Environmental Effects Monitoring (EEM) program (Lowell et al. 2005) and the National Council for Air and Stream Improvement's (NCASI) Long-Term Receiving Water Study (LTRWS) (Hall and Miner 1997; Hall et al. 2009), although other studies have also examined these endpoints (Culp et al. 2003, 2004).

The extensive body of effluent effects research on fish conducted since the 1990s has been reviewed and summarized by several authors (Hewitt, Parrott, and McMaster 2006; Hewitt et al. 2008; McMaster, Parrott, and Hewitt 2006; Parrott, McMaster, and Hewitt 2006; Dubé, Munkittrick, and Hewitt 2008). A variety of effluent effects have been observed, although reproductive effects have garnered the greatest attention. These include reduced gonad size, changes in the concentration and production of sex steroids and hormones, and changes in the expression of secondary sex characteristics. Among biomarkers typically examined, reduced egg production has shown the most consistent response to effluent exposure. Other responses seen in wild fish include changes in condition (i.e., length:weight ratios), shifts in age class structure, and an increase in weight at age (Munkittrick et al. 2002). Attempts have also been made to develop biomarkers that provide early and sensitive detection of effluent effects, such as measurements of the activity of fish liver detoxification enzymes known as mixed-function oxygenases (MFO).

Researchers have attempted to identify the causative factor and/or effluent constituent(s) for these observed biological responses. In the 1980s and 1990s, chemical characterization of effluent was developed to a degree (e.g. LaFleur 1996; LaFleur and Barton 2003). However, variations in manufacturing processes, wood furnishes, process derivatives, chemical additives, and biotreatment types and efficiencies make it impossible to make general assessments across mills. Some information has been gained from examining specific effluent compounds such as certain phytosterols, resin acids, and some additives, as well as changes in response following mill process changes. Researchers have concluded that effluents from all types of mill processes (e.g., mechanical pulping, deinking) are capable of affecting fish reproduction. Although process upgrades have typically improved effluent quality and biological response, the improvement cannot be attributed to a single modification because multiple process upgrades were implemented concurrently. The biological response of fish was often associated with reduced use of molecular chlorine, improved condensate handling, and control of spent liquor losses (Hewitt et al. 2008).

A key component of the pulping process is the recovery of spent pulping liquors for the recovery and reuse of chemicals and energy production. These pulping liquors have high concentrations of organic compounds, and although some systemic losses from the pulp mill and recovery systems occur via pulp washers, evaporators, knotting and screening systems, and other processes, it is estimated that 97 to 99.5% of weak black liquor is recovered (Carey, Hall, and McCubbin 2002). Additionally, spills due to upset conditions may result in black liquor losses beyond the 0.5 to 3% from systemic losses, which can upset treatment systems resulting in incomplete biotreatment, or increase the concentration of organic substances that are recalcitrant to treatment. Losses of green and white liquor produced by mills are also possible. However, these liquors have no bioactive organic components, and are presumably less toxic than black liquors.

Although there are clear relationships between effluent exposure and biological response, and liquor loss has been implicated in these responses, relatively few studies addressing the organic compounds associated with black liquor have been conducted. Further, no study has explicitly linked organic compounds in black liquor to in-stream patterns in effluent-exposed biological communities (Appendix A). Table 10.1 summarizes the findings to date from laboratory and field studies examining biological response in the context of exposure to effluent black liquor.

Table 10.1 Generalized Findings from Laboratory and Field Studies Examining Biological Response in Context of Exposure to Effluent Black Liquor

Study Type	Typical Endpoints	Generalized Findings
Laboratory studies	Enzyme biomarkers, sex steroids, reproduction	Effluent response often seen in enzyme biomarkers and (at least some) concentrations of sex steroids; reproductive changes (egg production, hatchability) not always seen
Artificial stream/mesocosm studies	Enzyme biomarkers, sex steroids	Effluent response often seen in enzyme biomarkers and (at least some) concentrations of sex steroids; reproductive changes (egg production, hatchability) not always seen
Caging studies	Enzyme biomarkers, sex steroids	Effluent response often seen in enzyme biomarkers and (at least some) concentrations of sex steroids; reproductive changes (egg production, hatchability) not always seen
Field studies	Physiological (enzyme biomarkers) to population/community	Effluent response often seen in enzyme biomarkers and sex steroids; some observed changes in organ size; population- and community-level response less common

11.0 MILL EXPERIENCES WITH IMPLEMENTING LIQUOR LOSS STRATEGIES

US mills required to implement spent liquor BMPs have taken a variety of approaches to meeting the regulatory requirement. In every case, the BMP plan is very specific to the site. Some mills have invested in site modifications to improve liquor loss management, but this is not a foregone conclusion. Development and implementation of standard operating procedures and periodic training are important aspects of a BMP program regardless of investments in modifications. It is also important to recognize that not all mills will be able to achieve the same level of performance, and the BMP program should be realistic in terms of what it can reasonably expect to achieve given basic process configurations and constraints.

The following information summarizes the BMP plans of four US bleached kraft mills, as provided to NCASI by companies representing facilities of different size and physical layout.

MILL A

Mill A produces printing and writing grades from softwood and hardwood pulps produced on separate fibrelines. The hardwood pulping system employs batch digesters and the softwood line uses a Kamyr continuous digester. Brownstock pulp washing systems include both diffusion and vacuum drum units. Brownstock is oxygen delignified and bleached in a three-stage ECF sequence. Spent pulping liquor is processed continuously through the chemical recovery system and storage tanks are employed to provide a temporary operating buffer between the fibrelines and the various steps in the recovery process including multiple effect evaporators, concentrators, finishers, and recovery furnaces. The mill skims soap from liquor in the evaporator trains and processes it through an acidulation plant to produce crude tall oil, which is sold. Turpentine collected from the softwood digester is decanted and sent to storage for eventual sale. The mill utilizes an ASB for secondary treatment. Discharge is to a small receiving stream and because of this, close attention is paid to ensuring that the effluent is of high quality at all times. This includes a well-developed system for minimizing spent liquor losses to sewer. Indeed, mill staff indicate that implementation of BMP is a significant reason behind environmental wastewater compliance and success at the facility, noting that source reduction is easier, less expensive, and more likely to help in maintaining compliance than "end-of-pipe" treatment.

An engineering analysis of the mill's spent liquor management systems and practices was conducted in 1999. The analysis reviewed the basic philosophy, engineered systems, work practices, and other aspects and identified specific requirements needed to comply with the BMP provisions of the Cluster Rule. The study also identified recommended improvements to further minimize potential losses of spent pulping liquor.

Engineered Controls and Containment Prior to Engineering Analysis

Digesters and Brown Stock Washing Areas

- Liquor losses from the process are avoided as much as possible with standard operating procedures, tank level management, and preventive maintenance.
- If liquor losses occur, they are contained within the area and directed to either the Kamyr digester area sump or the batch digesters area sump.
- The contents of both sumps are recovered if conductivity is high.
- Most tanks do not have high level alarms.
- Although the sumps are instrumented to recover on high conductivity, the operators are not alerted when material is being recovered, as there are no alarms for high conductivity in the sump, or pump operation.

Screening, Cleaning and Oxygen Delignification

- Liquor losses from the process are avoided as much as possible with standard operating procedures, tank level management, tank high level alarms, and preventive maintenance.
- Wash water added to the final post-oxygen delignification washers is managed based on preventing liquor losses instead of using the wash water to reach a target cleanliness of the pulp to the bleach plant. The mill applies a strict countercurrent washing philosophy to its filtrate use from post oxygen washing, through the screening deckers and back to the brownstock washers, with no intentional dumping of filtrate at any stage.
- If liquor losses occur, the operators are alerted through high level alarms on tanks, and remedial actions are initiated. Liquor losses are contained within the area and directed to the oxygen delignification sump.
- The contents of the sump are recovered at all times. The only exception to this is the drain from the top floor, which is diverted to effluent during high rain events.

- Seal water is segregated in the area, and bypasses the sump.

Evaporators and Recovery

- Liquor losses from the process are avoided as much as possible with standard operating procedures, tank level management, tank high level alarms, and preventive maintenance.
- Maintenance outages are scheduled and staggered so that all wash water can be contained and recovered within the existing liquor recovery capacity.
- Inspections of equipment, including conductivity meters, are performed frequently.
- If liquor cannot be processed or contained because of lack of liquor storage capacity, pulp production will be curtailed until the situation is resolved.
- If liquor losses occur, the operators are alerted through high level and overflow alarms on tanks, and remedial actions are initiated. Liquor losses are contained within the area and directed to either the evaporator sump or the recovery sump.
- The contents of both sumps are recovered if conductivity is high.
- Seal water is segregated in the area, and bypasses the sump.

Turpentine Area

- The turpentine processing area is curbed so as to direct any leaks or spills toward the Kamyr sump prior to discharge to the mill sewer.
- The turpentine storage tank is isolated with secondary containment for the storage tank capacity plus freeboard for precipitation.
- The turpentine loading area is not isolated from sewer, and any leaks or spills would be routed to effluent treatment via the storm water collection system.

Soap Processing Area

- The soap processing area is curbed in some areas, and any leaks or spills are directed toward a nearby drain which directs flow to a ditch which flows into the WWTP.
- The tall oil loading area is not isolated from sewer, and any leaks or spills are directed to the wastewater treatment system via the storm water collection system.

The engineering analysis identified the following practical recommendations for BMPs.

- Install a high conductivity alarm on the Kamyr and batch digester sumps, so that the operators are made aware of high conductivity events, and so that they can verify that the sump pumps are recovering the material to process.
- Construct containment to isolate the turpentine processing area, including the turpentine condenser, decanter, reflux tank, and condensate feed tank from the U-drain system and prevent spills from flowing directly to sewer.
- Implement procedures (SOPs) for draining the (isolated) turpentine processing area, turpentine storage area, soap processing and storage area, and the tall oil processing and storage area.

- Implement formal procedures (SOPs) for performing tours of the operating areas for spills or losses identification.
- Construct containment to isolate the turpentine storage tank underflow pump.
- Construct containment to isolate the turpentine loading area from sewer.
- Modify sumps and U-drains within the soap skimmer and soap storage tank containment area, to isolate area from sewer.
- Isolate tall oil process area with a recovery sump and recover contents to waste acid tank.
- Isolate tall oil loading area, draining to tall oil process area recovery sump.

The following projects were identified as presenting opportunities for system improvements in addition to reducing spent liquor losses upstream of the wastewater treatment system.

- Add high level alarms on main storage tanks in the batch and Kamyr digester areas, to help prevent spills.
- Raise the curbing between the two 15% black liquor storage tanks to provide a minimum height of 6" above grade, to contain leaks and direct material to a sump for recovery.
- Complete the curbing along the remainder of the west perimeter and add 6" curbing along the entire north perimeter of the heavy liquor storage tank area, to contain leaks and direct material to the evaporator sump for recovery.
- Add curbing around black liquor and fuel pumps near the southwest corner of the recovery boiler building to divert spills and leaks to U-drain in precipitator area. This will ensure that spills are contained in the pad area, and directed to the recovery sump, to be recovered to process.
- Implement formal procedures (SOPs) for maintaining conductivity meters and other monitoring devices critical for avoiding or recovering liquor spills.
- Implement procedures (SOPs) for operating departments to communicate occurrences of liquor losses to sewer to the environmental department.
- Add high level alarms to tall oil process area storage tanks.

Monitoring

In addition to conductivity monitoring in process areas, the mill monitors the overall mill wastewater on a daily basis to determine if trends in liquor losses are statistically significant and to trigger corrective and/or investigative actions. Composite samples are analyzed daily for total organic carbon (TOC) and the values are tracked using a Shewhart process control chart. Action levels were calculated based on an initial seven-month period of data that was log-transformed and corrected for autocorrelation and screened to remove values exceeding 3 Sigma. The lower action level which triggers an investigation was set at 2 Sigma above the mean; the upper action level which triggers correction action was set at 3 Sigma above the mean.

Work Practices

An important aspect of the liquor loss management program at Mill A is the use of work practices to avoid spills or to minimize unintentional spills and leaks before they occur. These include standard operating procedures, preventive maintenance, surveillance, and repair programs for areas and equipment items in spent pulping liquor, turpentine, and soap service.

Standard operating procedures (SOPs) are used in all areas containing equipment in spent pulping liquor, soap, and turpentine service, to minimize unanticipated losses to sewer. These work instructions are available to operating personnel through a computer database. The SOP system is complemented with regular training for area operators, and there is a formal annual liquor loss BMPs training program in place. Operators are trained in the specifics of operating and monitoring individual pieces and systems of equipment, including procedures necessary for safe operation and to maintain environmental compliance. In addition, operators are trained in operating process systems to minimize black liquor losses to the wastewater treatment system.

A system of preventive maintenance is in place to proactively identify and address equipment items in need of attention, and to minimize equipment failure occurrences. Equipment items included in the preventive maintenance program include all process vessels, storage tanks, pumping systems, instrumentation, evaporators, heat exchangers, recovery boilers, pipelines, valves, fittings, or other devices that transport or come into contact with spent pulping liquor, turpentine, or soap. The preventive maintenance system in place at the mill encompasses the pulping area and the utilities and recovery area, as described below.

Mill A conducts visual inspections at least annually of spent liquor bulk storage tanks and other spent liquor tanks that do not have secondary containment structures. Ultrasonic testing of wall thickness is typically conducted every 2 to 4 years on spent liquor bulk storage tanks.

A system of surveillance and repair is used to complement the preventive maintenance program, to identify any unanticipated equipment problems, and repair them as soon as possible. Equipment items in the surveillance and repair program include all process vessels, storage tanks, pumping systems, evaporators, heat exchangers, recovery boilers, pipelines, valves, fittings, or other devices that transport or come into contact with spent pulping liquor, turpentine, or soap.

For example, in the pulping and recovery areas, the operators inspect each area at least once per shift. Exceptions are noted on an environmental logsheet in each area. When leaks are detected which require immediate attention, the maintenance crew may be contacted by telephone or radio. Non-emergency repairs are requested using the mill's work notification system. After repairs are complete, the maintenance employee records the equipment number, date, and action taken. This information is then entered into a computer-based maintenance management system. This system is used to track repairs and schedule preventive maintenance.

Leaks are repaired immediately, if possible, by maintenance personnel. If the repair cannot be carried out during the regularly scheduled maintenance time, and is not of an urgent nature, it is scheduled to be performed as soon as possible, based on priority. If it is not possible to make repairs during normal operations, temporary means for mitigating leaks are provided and repairs scheduled for the next maintenance outage.

The environmental department conducts initial training and annual refresher training for mill supervisors, operators, maintenance crews, and process engineers from the affected process areas.

The initial training session includes the following topics:

- overview of pertinent regulations;
- description of liquor loss and spill control, detection and recovery equipment installed;
- inspection requirements;

- repair and mitigation requirements;
- monitoring and action levels; and
- notification and reporting procedures.

The annual refresher training includes the following topics:

- regulatory review;
- spill history (spill events and action level exceedances);
- equipment and process modifications; and
- summary of effluent monitoring results.

The mill has guidelines that ensure potential environmental impacts are considered before making any changes to the mill processes, procedures, or equipment. The program is applicable to all capital jobs (other than direct replacement) with a cost above $10,000. The environmental staff reviews the potential environmental impacts of each project and verifies that proper BMP procedures will be followed when spent liquor, soap, or turpentine systems will be affected by the project in question.

The mill also has a procedure in place to ensure that mill trials and process modifications are reviewed for environmental compliance and impacts. Trials and temporary process modifications require a Mill Trial Authorization form, which must be signed by the mill environmental department. The environmental staff reviews the trial plan for BMP compliance and spill potential.

MILL B

Mill B is an integrated bleached papergrade kraft mill. Pulping consists of one hardwood line and one softwood line. The hardwood line consists of batch digesters, a knotter, three stages of washing, primary and secondary screening, and a high density storage tank.

The softwood line includes a single Kamyr continuous digester and blow tank, pressure knotter, two stages of brownstock washing, an oxygen delignification stage and blow tank, two stages of post-oxygen washing, a pressurized screening system and a high density storage tank. Turpentine is collected and decanted.

Black liquor is sent to two sets of six effect evaporators that increase the black liquor solids from approximately 15% to 48%. Soap is intermittently skimmed off the top of the 48% black liquor tanks and is burned in the recovery boiler. The evaporators are followed by a concentrator which increases the black liquor solids from about 48% to 75%.

The wastewater treatment system includes primary clarification and secondary treatment in an activated sludge system. Discharge is to a small receiving stream.

Mill B’s liquor loss management program includes engineered systems, operating and maintenance procedures, tank integrity testing, training, monitoring, reporting, and construction review provisions. The engineered systems in each of the process areas are described below.

Hardwood Fibre Line/Evaporator Area

The liquor building includes the hardwood digester blow tank, hardwood hot water tank, black liquor tanks, and white liquor tanks. Any leaks and spills from these equipment items or other items in the building would flow to the basement, where a floor drain would route the material to the digester basement sump. The digester building includes nine batch digesters, heat exchangers, and black liquor circulating pumps. Any leaks and spills from this equipment or other equipment items in the building would be routed, via a series of floor drains, to the digester basement sump pit. The digester basement sump pump (based on sump pit level) would pump the spill back into the process at the liquor collection tank.

Any spills or leaks in the hardwood fibreline area are collected in the pulp mill process sewer. The sewer is equipped with a system to return leaks/spills back to the system based on conductivity. If the conductivity is high (indicating black liquor) the flow is sent to the hardwood black liquor tank. Additionally, any overflow from the knotters goes to a collection sump and is pumped to the hardwood black liquor tank. The old filtrate tanks can be used for additional capacity if the hardwood black liquor tank is full.

If the conductivity of the hardwood digester heat exchanger steam condensate is high, it will be returned to the liquor cycle. In the case of low conductivity, the steam condensate is sent to the hardwood hot water tank to be used for washing.

The evaporator building uses a system that is similar to the collection systems of the liquor and digester buildings. Any leaks and spills from the south side of the building would be routed, via a series of floor drains, to the No. 1 evaporator sump pit. The pit is equipped with a continuous conductivity monitor. If high conductivity is detected, the material is sent back to the process. Otherwise, the flow is sent to the pulp mill sewer. Any leaks and spills from equipment in the north side of the building would be routed, via a series of floor drains, to the No. 2 evaporator sump pit. Spillage in the No. 2 evaporator sump would then flow by gravity to the No. 1 sump pit.

The ground around the evaporator feed tanks is paved and has a retaining wall. This improvement contains any leaks and spills from the tanks and associated pipes, routing spillage to the evaporator sump pit. The evaporator sump returns any spillage, based on conductivity, back to the process.

Prior to 2001, the No. 2 evaporator sump pump did not have any conductivity monitors or the ability to divert high conductivity flows. Following the modifications, the No. 2 evaporator sump pump now has the ability to divert flows back to the process rather than sending them to the sewer.

A conductivity sample point and diversion valves have been installed for the hardwood digester sump pump. The pump now has the ability to divert flows based on conductivity. This will allow high conductivity flows to be diverted back to the process rather than being sent to the sewer and waste treatment.

Changes were made to the diversion system for the No. 1 evaporator surface condenser to improve its performance during June 2002. On a diversion, the condensate will go to the evaporator basement, which will in turn cause the condensate to be diverted to the black liquor system when it is contaminated.

Three new diversion systems were added to the foul condensate collection system. The No. 2 evaporator surface condenser now diverts to the seal tank in the No. 1 evaporator basement based on conductivity. The non-condensable gas vent condenser condensate is diverted to the evaporator black liquor feed tanks based on conductivity. In addition, the combined evaporator ejector condenser condensate also diverts back to the black liquor feeds tanks based on conductivity.

Provisions were added to provide the ability to pump from the foul condensate collection tank back to the black liquor cycle in the event that the condensate would become contaminated with black liquor.

Softwood Fibre Line/Turpentine System

Spent pulping liquor is recovered from the softwood knotter rejects. The rejects are placed in a draining dumpster on a concrete pad at the north side of the oxygen delignification building. The pulping liquor drains out of the bottom of the dumpster and flows by gravity to a floor drain. It is then routed by gravity to a sump collection pit. The collection sump then pumps the liquor back into the softwood fibre line pulping process.

A system was added to the softwood fibre line to provide the capability to return leaks and spills to the process. The system includes a sump pump and continuous conductivity monitor, similar to the systems in place in the hardwood fibre line and concentrator areas.

The turpentine decanter and storage tank have full secondary containment. It is not desirable to return any spilled or leaked turpentine back to the process. Therefore, the containment area is equipped with a sump pump that can pump any spillage to the process sewer at a slow rate that will not disrupt the wastewater treatment plant.

A new system to contain leaks and spills at the turpentine loading area has been installed. The system consists of spill trays under the rail cars and a concrete pad between the storage tank and the railroad tracks. Any spillage is directed by gravity to the turpentine storage tank secondary containment area.

Concentrator/Recovery Areas

Any spills and leaks in the concentrator and recovery buildings are returned to the process. Spillage from the concentrator building is routed to the concentrator sump pit, and spillage from the recovery building is routed to the recovery sump pit. The sump pumps in both pits are equipped with conductivity monitors. Therefore, if the conductivity is high in either case, the spillage is pumped back into the process at the 15% black liquor tank. The black liquor mix tank is equipped to prevent a spill caused by overfilling. The overflow line on the tank is routed to the dump tank which is part of the process.

The yard tanks are also equipped with an overflow line. The overflow goes to the No. 1 evaporator sump pit, which is equipped with a conductivity monitor. If the conductivity is high, the overflow would be pumped back to the yard tanks, which can subsequently be pumped to the 15% black liquor tanks.

The evaporator feed tanks also have an overflow line that goes to the No. 1 evaporator sump. Based on conductivity, the overflow would be pumped to the yard tanks.

The black liquor mix tank is part of the recovery boiler process and is located inside the recovery boiler building. Any leaks from the tank would go to the recovery sump. The tank overflow line goes to the dump tank.

The dump tank is also part of the recovery process. Process flows from this tank can be routed to either the 48% or 15% black liquor tanks. This tank is inside the recovery building; therefore, any leaks and spills from it would be pumped by the recovery sump back to the process.

Black Liquor Tanks

In addition to the black liquor tanks described above, Mill B has two 48%, one 75%, and two 15% black liquor tanks. Both of the 48% black liquor tanks are equipped with 5" curbing that can route small leaks to a sump pump which sends the flow to the old recovery sump. The old recovery sump pump will pump the flow to the No. 1 evaporator sump which will (based on conductivity) pump the spillage back into the process.

The 75% black liquor tank is equipped with an overflow that goes to the dump tank. The bottom of the tank is enclosed, routing any spills from the bottom of the tank to the old recovery sump.

The mill maintains two 15% weak liquor tanks. The bases of the tanks are approximately five feet up on a concrete platform. The platforms are equipped with curbing around the tanks (7" deep, 10" wide) that routes any small leaks and spills to the Kamyr floor channel drain. The tanks are connected by piping to equalize the levels. A blacktop rise has been installed on the nearby ground to direct any larger spills away from a nearby storm sewer drain.

MILL C

Mill C is a bleached kraft market pulp mill that uses three continuous digesters, one line with three brownstock washers, and a single recovery furnace. An engineering analysis conducted by the mill served as the basis for the BMP plan. In general, the plan involves preventing losses from the process areas, recovering any significant losses within the pulping and recovery process areas when they occur, and diverting any losses that get as far as the main sewer to an emergency spill pond that can be used to meter lost material to the wastewater treatment plant at a controlled rate. Most of the equipment was already in place when the BMP plan was developed.

The mill uses conductivity meters to monitor the process sewers for spills and leaks. The conductivity meters allow the diversion and recovery of spilled or leaked black liquor. In the power and recovery department, conductivity meters are located in the process sewers that serve the floor drains near the evaporators and the floor drains near the liquor storage tanks. These sewers normally drain to the wastewater treatment system. If the conductivity meter indicates that a spill has occurred (1,800 µmhos/cm or higher), a gate is activated, allowing the material to drain into a sump of 86,000 gallon capacity, from which it can be pumped back into the liquor system until the conductivity drops below the setpoint.

Under normal conditions in the pulp mill, floor drains and process sewers flow through the pulp mill sump (10,500 gallon capacity) which normally drains to the main sewer leading to the wastewater treatment system. A conductivity reading of 1,750 µmhos/cm sustained for 10 minutes will automatically cause the sump contents to be pumped to the collection tank (360,000 gallon capacity) instead.

The 50% black liquor storage tank has secondary containment. Mill staff performs annual visual inspections and non-destructive testing for tank thickness every 3 to 5 years on all spent liquor tanks.

The mill has curbs and dikes around the black liquor handling tanks to direct spills and leaks into the pulp mill or evaporator/recovery area sewers, where any spill can be detected by conductivity probes and reclaimed as described above. All spent liquor tanks are equipped with high level alarms to alert the operator of imminent overflows.

The mill also has an emergency settling pond (ESP) which holds approximately 5 million gallons. The mill effluent main sump could be diverted to the ESP for approximately 13 hours before filling the pond.

The effluent reaching the wastewater treatment system consists of acidic and alkaline streams. The alkaline streams are processed in a clarifier to remove settleable solids and then mixed with the acid streams. The pH of the mixture is adjusted and discharged to the secondary treatment plant for biological treatment.

The main sump and effluent clarifier are monitored by taking grab samples every four hours and testing for colour, conductivity, and pH. The main sump is diverted from the effluent clarifier to the

ESP if the effluent colour exceeds 1,800 colour units or the conductivity exceeds 4,000 μmhos/cm. After the event has passed, the ESP is slowly drained back to the main sump.

Mill staff conducts a routine monitoring program to assess organic loading trends and operating condition of the biological treatment system. Their BMP monitoring program uses colour measurements on 24-hour composite samples to track the overall liquor loss management performance. Action levels are set at the average plus two times the standard deviation (trigger for an investigation) and the average plus three times the standard deviation (trigger for corrective action), based on a six-month monitoring period used to establish a baseline.

Other aspects of Mill C's BMP plan include initial and refresher training sessions, standard spill reporting protocols and forms, plan review and update provisions, recordkeeping requirements, equipment maintenance logging, and others.

MILL D

Mill D is a bleached kraft mill making pulp and paper from softwood and hardwood furnishes that are cooked in continuous digesters. The BMP plan document establishes that the principle objective of the management systems, practices, and procedures described therein is to prevent significant losses and spills of spent pulping liquors from the immediate process areas. It goes on to state that the secondary objective is to control the rate of discharge of significant losses and spills of spent pulping liquor that do occur to protect the integrity of the wastewater treatment plant operation and receiving stream. Regarding liquor loss and spill prevention, the following measures were identified as being key to success.

- Appropriate standard operating procedures are in place and employees have received training in the objectives and practices.
- Process equipment is inspected regularly and maintained. Repair records are used to identify areas of high risk.
- Spill prevention systems (for example, high tank level alarms) are installed at important locations where significant losses can occur.

The following measures were identified as being key to the success of meeting the secondary objective of containment and control.

- Continuous, automatic monitoring systems are maintained to detect and control leaks, spills, and intentional diversions of spent pulping liquor from equipment in service. These monitoring systems are integrated with the mill process control system and include process area sewer and wastewater treatment plant conductivity monitors.
- Skilled operations staff investigates unusual operating conditions in process sewers, and corrective actions are taken to return unusual conditions to normal state.

An engineering analysis identified the significant equipment in the mill, primarily spent liquor tanks and the kraft digester systems, defined by a capacity to result in spent liquor flowing to sewer in a volume that could negatively impact the wastewater treatment system. The analysis identified a few new provisions that were added to the mill: additional curbing to route spills to area sewers, a permanent monitoring station at the treatment plant, one additional conductivity monitor in the recovery area, and procedures to enhance the use of weak black liquor storage tanks for recovering spills. Overall, the strategy, in order of preference, is to

- manage spent liquor at the source by utilizing standard operating procedures and spill prevention procedures;
- return spent liquor directly into the process to the maximum extent practicable; and
- divert wastewater containing higher than normal amounts of spent liquor to a holding basin so that it can be metered into the wastewater treatment plant at rates within the plant's assimilative capacity.

Initially, the mill used COD as its performance monitoring parameter, measured at the wastewater treatment plant. Recently, the mill changed to conductivity monitoring, as it was felt to be a better performance indicator, and therefore a better management tool because there is no delay in feedback as was the case with COD. Action limits were developed for COD initially, and later for conductivity.

Other aspects of Mill D's BMP plan include outline of employee training sessions, equipment inspection and leak repair guidelines, spill reporting protocols, plan review and update provisions, recordkeeping requirements, equipment maintenance logging, and others.

12.0 SUMMARY

This report provides an overview of a systematic analysis that individual facilities may apply to mitigate and minimize low-concentration spent liquor losses. While all mills in Canada have site-specific plans for dealing with acute spills, the more systemic losses of spent liquor inherent with the process have historically been more challenging to identify and minimize.

For the past decade or so, chemical pulping facilities in the US have applied best management practices (BMPs) and strategies for minimizing and/or recovering spent pulping liquor losses within the mill process. These actions have both reduced the load on the wastewater treatment system and reduced the day-to-day variability in untreated wastewater load, leading to more stable treatment system performance. During this time, the industry has also invested billions of dollars in other process modernization and improvement projects, many of which have resulted in significant reductions in spent pulping liquor losses.

Practical constraints to designing effective BMPs relate largely to the existing physical layout of individual facilities, along with the size and capacity of associated capital equipment. Financial and operational constraints relate to harnessing the creativity of facility staff, both engineering and operations, to systematically design a site-specific BMP program at low cost, with senior management support. Aspects that can help optimize BMP design include involving process operators in identifying low- or no-capital cost approaches that they would consider optimal for managing the process to minimize unnecessary releases of spent pulping liquor to sewer, with focus on reducing low-level background losses inherent to the process rather than acute spills.

The systematic BMP engineering approach presented in this report may prove useful for facilities currently working to address residual effects measured through Canada's EEM program or to address local receiving environment initiatives. The approach does not so much require pinpointing and minimizing specific substances of concern to the receiving environment, but allows for broadly applied process optimization strategies that seek to leverage the facility's current capabilities—both of equipment and of personnel—for an overall reduction in losses of organic material to the environment.

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APPENDIX A

EFFLUENT EFFECTS STUDIES SUMMARY TABLE

Effluent Effects Studies Summary Table

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Laboratory Studies							
Eel	*Anguilla anguilla*	BKME	Enzyme biomarkers	≤ 3 d	+	>6.25%	Pacheco & Santos 1999
Eel	*A. anguilla*	BKME	Stress parameters	≤188 h	+	50%	Santos & Pacheco 1996
Goldfish	*Carassius auratus*	BKME	Enzyme biomarkers	28 d	+	>50%	Diniz et al. 2009
Goldfish	*C. auratus*	BKME	Enzyme biomarkers		+	50%	Diniz et al. 2010
Goldfish	*C. auratus*	BKME	Enzyme biomarkers, histopathology	21 d	+	>50%	Diniz et al. 2011
Goldfish	*C. auratus*		Sex Steroids	≤20 d			McCarthy et al. 2003
Goldfish	*C. auratus*	BSME, BKME, and TMP (Canada)	Sex Steroids	16-21 d	-	100% (following upgrades)	Parrott et al. 1999
Goldfish	*C. auratus*	BSME, BKME, and TMP (Canada)	Sex Steroids	≤20 d	+	>25%	Parrott et al. 2000a
Spotted murrel	*C. punctatus*	Paper mill (India)	Immune endpoints	15-90 d	+	1%	Fatima et al. 2001
European whitefish	*Coregonus lavaretus*	BKME (Tasmania)	Physiological parameters	30 d	+	3.50%	Soimasuo et al. 1998b
European seabass	*Dicentrarchus labrax*	BKME	Enzyme biomarkers, histopathology	21 d	+	>25%	Diniz et al. 2011
European seabass	*D. labrax*		Enzyme biomarkers	6-72 h	+	>3.12%	Gravato & Santos 2002
Mummichog	*Fundulus heteroclitus*	BKME (Canada)	Reproductive endocrine function	30-57 d	+	1-5%	Dubé & MacLatchy 2000a
Mummichog	*F. heteroclitus*	BKME (Canada)	Testosterone	7-21 d	+	1%	Dubé & MacLatchy 2001
Mummichog	*F. heteroclitus*	BKME	Testosterone	7 d	+		Hewitt et al. 2002
Mummichog	*F. heteroclitus*	BKME	Reproductive endocrine function	7 d	+		MacLatchy et al. 2004
Common jollytail	*Galaxis maculatus*	Eucalypt-based pulp mill	Enzyme biomarkers, histology, organ size	7-12 w	+		Woodworth et al. 1998
Mosquitofish	*Gambusia affinis*	BKME/TMP (New Zealand), BKME and TMP (Canada)	Masculinization	21 d	-		Bandelj et al. 2006

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Laboratory Studies (continued)							
Mosquitofish	*G. affinis*	not stated	External characteristics	21 d			Ellis et al. 2000
Mosquitofish	*G. affinis*	BKME/TMP (New Zealand)	Masculinization, reproductive behavior	21 d	+	100%	Ellis et al. 2003
Three-spined stickleback	*Gasterosteus aculeatus*	Primary BKME (Sweden)		42 d	+	10%	Katsiadaki et al. 2002
Three-spined stickleback	*G. aculeatus*	BKME (St. Maurice R., QC, Canada)	Sex Steroids, enzyme biomarkers	7-21 d	+	≥10% at longer exposures	Wartman et al. 2009
Stinging catfish	*Heteropneustes fossilis*	Paper mill	Hematology	90 d	+	≥0.5%	Ahmad et al. 1998
Channel catfish	*Ictalurus punctatus*	BKME	Enzyme biomarkers	14 d	+		Mathermihaich and Digiulio 1991
Bluegill sunfish	*Lepomis macrochirus*	BKME	Hematology	56 d	-		D'Surney et al. 2000
Bluegill sunfish	*L. macrochirus*	UKME	Organ size and biochemical	30 d	-		Felder et al. 1998
Largemouth bass	*Micropterus salmoides*	BKME (Staulkinghead Cr., Bastrop, LA, USA)	Physiological and hematological endpoints	35 d	+		Baer et al. 2009
Largemouth bass	*M. salmoides*	BKME	Messenger RNA	7 d			Denslow et al. 2000
Largemouth bass	*M. salmoides*		Enzyme biomarkers, sex steroids	7-56 d	variable		Denslow et al. 2004
Largemouth bass	*M. salmoides*	BKME and KME (USA)	Sex steroids, histopathology, organ size	28-56 d	variable	≥20%	Sepúlveda et al. 2001
Largemouth bass	*M. salmoides*	BKME and KME (USA)	Sex steroids, organ size	28-56 d	+	≥10%	Sepúlveda et al. 2003
Striped bass	*Morone saxatilus*	BKME (Blackwater R., VA)	Survival and growth	20 d	-		Burton et al. 1984
Fourhorn sculpin	*Myoxocephalus quadricornis*	BKME		5-9 mo	+		Hardig et al. 1988
Various (Pacific salmon)	*Oncorhynchus gorbuscha, O. kisutch, & O. nerka*	BKME	96-h LC50	96 h	variable	≥22-100%	Davis & Mason 1973
Coho salmon	*O. kisutch*	KME	Hematology	12 h, 25 d	-		McLeay 1973

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Laboratory Studies (continued)							
Rainbow trout	*Oncorhynchus mykiss*	BKME and TMP (New Zealand)	Growth and reproductive endpoints	2-8 mo	variable		Ellis et al. 2005
Rainbow trout	*O. mykiss*	BKME/TMP	Critical swimming speed, O2 consumption, and hematology	4 w	variable	70%	Landman et al. 2006
Rainbow trout	*O. mykiss*	Various (13 mills)	Enzyme biomarkers	4 d	-		Martel & Kovacs 1997
Rainbow trout	*O. mykiss*	BKME	Enzyme biomarkers, sex steroids, organ size	4.5 mo	variable		Mattson et al. 2001
Rainbow trout	*O. mykiss*	BKME (Grande Prarie, AB, Canada), BSME (Edmunston, NB, Canada)	Enzyme biomarkers, sex steroids	21 d	+		Oakes et al. 2005b
Rainbow trout	*O. mykiss*	BKME	Enzyme biomarkers, sex steroids	21 d	+		Tremblay & Van Der Kraak 1999
Rainbow trout	*O. mykiss*	BKME and TMP (New Zealand)	Growth and reproductive endpoints	2-8 mo	+	12%	van den Heuvel & Ellis 2002
Rainbow trout	*O. mykiss*		Growth, sex steroids, and hematology		-		van den Heuvel et al. 2008
Chinook salmon	*Oncorhynchus tshawytscha*	BKME (Southern British Columbia, Canada)	Sex determination and differentiation	29 d	+	100%	Afonso et al. 2002
Chinook salmon	*O. tshawytscha*	BKME (Southern British Columbia, Canada)	Stress parameters	30 d	+	≥1%	Afonso et al. 2003
Chinook salmon	*O. tshawytscha*	BKME (Fraser R., Prince George, BC, Canada)	Gill morphometry and hematology	28 d	+	16%	Kruzynski et al. 2004
Chinook salmon	*O. tshawytscha*	BKME (Fraser R., BC)	Survival and growth, hematology, organ size, enzyme biomarkers	144 d	variable	most endpoints unchaged with effluent exposure	Servizi et al. 1993
Chinook salmon	*O. tshawytscha*	BKME	Enzyme biomarkers	28 d	+	>16%	Wilson et al. 2001
Tilapia	*Oreochromis mossambicus*	BKME	Enzyme biomarkers, organ size	3-7 d	variable		Chen et al. 2001
Fathead minnow	*Pimephales promelas*	BKME (USA)	Growth, reproduction	75 d	variable	100%	Borton et al. 2004

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Laboratory Studies (continued)							
Fathead minnow	*P. promelas*	BKME (Codorus Cr., PA; Leaf R., MS; Willamette R., OR), UKME (McKenzie R., OR)	Survival, growth, organ size, reproduction	5-6 mo	variable	>8%	Borton et al. 2009
Fathead minnow	*P. promelas*	BKME (Canada)	Growth, reproduction	7-275 d	variable	≥2.5%	Kovacs et al. 1995
Fathead minnow	*P. promelas*	BKME	Growth, reproduction	≤180 d	-		Kovacs et al. 1996
Fathead minnow	*P. promelas*	BKME (n=2), TMP (n=2), and MP (n=1; Canada)	Sex steroids, organ size, reproduction	21 d	variable		Kovacs et al. 2005
Fathead minnow	*P. promelas*	TMP	Sex steroids, organ size, reproduction	5-6 d	variable		Kovacs et al. 2007
Fathead minnow	*P. promelas*	BKME (n=7; Canada)	Reproduction	5 d	variable		Kovacs et al. 2011
Fathead minnow	*P. promelas*	BKME (n=2), TMP (n=2), and MP (n=2; Canada)	Sex steroids, organ size, reproduction	28 d	variable	20%	Martel et al. 2004
Fathead minnow	*P. promelas*	BKME, TMPE	Sex steroids, organ size, reproduction	21 d	-		Martel et al. 2008
Fathead minnow	*P. promelas*	BKME (Eastern Canada)	Reproduction	5 d, 21 d	variable	>20 mg/L	Martel et al. 2011
Fathead minnow	*P. promelas*	BSME (Canada)	Growth, reproduction	125 d	variable		Parrott & Wood 2002
Fathead minnow	*P. promelas*	BSME	Growth, reproduction				Parrott et al. 2000b
Fathead minnow	*P. promelas*	BSME (Canada)	Growth, reproduction	125 d	+	≥3.2%	Parrott et al. 2003
Fathead minnow	*P. promelas*	BSME (St. John R., Canada)	Growth, reproduction	140 d	+	≥10%	Parrott et al. 2004
Fathead minnow	*P. promelas*	BKME (St. Maurice R., QC, Canada)	Growth, reproduction		+	≥1%	Parrott et al. 2010
Fathead minnow	*P. promelas*	BKME, TMP	Gene expression	5 d	variable	100%	Popesku et al. 2010
Fathead minnow	*P. promelas*	BKME (Jackfish Bay, ON, Canada)	Growth, reproduction	21 d	variable	≥1%	Rickwood et al. 2006a
Fathead minnow	*P. promelas*	BKME (Jackfish Bay, ON, Canada)	Growth, reproduction	21 d	variable		Rickwood et al. 2006b
Fathead minnow	*P. promelas*	Combined news and kraft pulp and paper mill (ON, Canada)	Reproduction, sex steroids, and enzyme biomarkers	6 d	+		Werner et al. 2010
Guppy	*Poecilia promelas*	BKME (Sweden)	Masculinization, enzyme biomarkers	42 d	+	10%	Larsson et al. 2002

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Laboratory Studies (continued)							
Roach	*Rutilus rutilus*	BKME (Finland)	Enzyme biomarkers, immune endpoints	21 d	variable	20%	Aaltonen et al. 2000a
Roach	*R. rutilus*	Various	Immune endpoints	5 w	variable	0.6-2%	Aaltonen et al. 2000b
Roach	*R. rutilus*	BKME (Lake Vatia, Finland)	Hematology	72 h	+		Jeney et al. 1996
Artificial Stream/ Mesocosm Studies							
White sucker	*Catostomus commersoni*	BSME/groundwood	Enzyme biomarkers	4-20 d	+	50%	Hewitt et al. 2003b
European whitefish	*Coregonus lavaretus*	BKME (Finland)	Enzyme biomarkers	3-6 w	variable		Lappivaara 2001
Channel catfish	*Ictalurus punctatus*	BKME	Enzyme biomarkers	263 d	+	≥4%	Bankey et al. 1995
Rainbow trout	*O. mykiss*	BKME	Growth, survival, histopathology	6-9 mo	variable		Haley et al. 1995
Rainbow trout	*O. mykiss*	BKME	Histopathology	10-42 mo	-		Hall et al. 1992
Rainbow trout	*O. mykiss*	BKME (Sweden)	Enzyme biomarkers	50 d	+	2%	Lindesjöö et al. 2002
Rainbow trout	*O. mykiss*	BKME, TMP	Growth, organ size, sex steroids	2 mo	variable	10%	van den Heuvel et al. 2002
Fathead minnow	*Pimephales promelas*	BKME (Wabigoon R., Dryden, ON)	Sex steroids	54 d	+	60%	Pollock et al. 2010
Brown trout	*Salmo trutta*	TMP	Enzyme biomarkers, histopathology, hematology	8 w	variable	0.50%	Johnsen et al. 1998
Brown trout	*S. trutta*	Mechanical (location not stated)	Sex steroids, reproduction	4 mo	variable		Johnsen et al. 2000
Caging Studies							
Eel	*Anguilla anguilla*	BKME	Enzyme biomarkers	3 d	+		Pacheco & Santos 1999
Eel	*A. anguilla*	BKME	Enzyme biomarkers	8 and 48 h	+		Santos et al. 2006
Shortfin eel	*Anguilla australis*	BKME, TMP, and CTMP (New Zealand)	Sex Steroids, enzyme biomarkers, hematology	21 d	+		van den Heuvel et al. 2006
Goldfish	*C. auratus*	BKME (Terrace Bay, ON)	Sex steroids	Up to 16 d	+	~50%	McMaster et al. 1996b

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Caging Studies (continued)							
Crucian carp	*Carassius carassius*	BKME (Finland)	Sex steroids, organ size, histology		+	100%	Kukkonen et al. 1999
White sucker	*C. commersoni*	BKME (St. Maurice R., QC, Canada)	Sex steroids	72 h	+		Gagnon et al. 1994a
White sucker	*C. commersoni*	BKME (Terrace Bay, ON)	Enzyme biomarkers	4 d	+		Hewitt et al. 2000
European whitefish	*Coregonus lavaretus*	BKME (S. Lake Saimaa, Finland)	Enzyme biomarkers, sex steroids	1 month	+		Karels et al. 1999
European whitefish	*C. lavaretus*	BKME	Stress parameters	30 d	+		Lappivaara et al. 2002
European whitefish	*C. lavaretus*	Various (S. Lake Saimaa, Finland)	Sex steroids		variable		Mellanen et al. 1999
European whitefish	*C. lavaretus*	BKME (Lake Saimaa, Finland)	Enzyme biomarkers	1 month	+		Soimasuo et al. 1995
European whitefish	*C. lavaretus*	Various	Enzyme biomarkers, sex steroids	30 d	+		Soimasuo et al. 1998a
Tomcod	*Microgadus tomcod*	BKME (Miramichi R., NB, Canada)	Enzyme biomarkers		+		Courtenay et al. 1993
Rainbow trout	*O. mykiss*	Biobio R., Chile	Enzyme biomarkers, sex steroids	30 d	+		Orrego et al. 2006
Field Studies							
White sturgeon	*Acipenser transmontanus*	BKME and non-pulp-mill sources (Columbia R., Washington)	Sex steroids, organochloride burden		variable		Foster et al. 2001
Brown bullhead	*Ameirus nebulosis*	BKME (Waikato R., New Zealand)	Sex steroids, organ size, reproduction, enzyme biomarkers, hematology, population measures		variable		West et al. 2006
Goldfish	*C. auratus*	BKME (New Zealand)	Histopathology		+		Lindesjöö & Thulin 1994
Goldfish	*C. auratus*	BKME (Waikato R., New Zealand)	Fin erosion		+		Sharples et al. 1994
Longnose sucker	*C. catostomus*	Peace/Athabasca/Slave R., Canada	Sex steroids		+		Cash et al. 2000

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Field Studies (continued)							
Longnose sucker	*C. catostomus*	BKME (Wapiti/Smokey R., AB, Canada)	Sex steroids, organ size, enzyme biomarkers, hematology, population measures		+		Kloeppersams et al. 1994
Longnose sucker	*C. catostomus*	BKME (Jackfish Bay, ON, Canada)	Sex steroids, enzyme biomarkers		+		Munkittrick et al. 1992b
Longnose sucker	*C. catostomus*	BKME (Jackfish Bay, ON, Canada)	Sex steroids, gonad size		variable		Munkittrick et al. 1998
Longnose sucker	*C. catostomus*	BKME (Wapiti/Smokey R., AB, Canada)	Population measures		variable		Swanson et al. 1994
White sucker	*Catostomus commersoni*	BKME (Jackfish Bay/Moose R., ON, Canada)	Sex steroids, gonad size, reproductive characteristics	17 y	variable		Bowron et al. 2009
White sucker	*C. commersoni*	BKME (St. Maurice R., QC, Canada)	Growth, gonad size, reproductive characteristics		+		Bussiéres et al. 1998
White sucker	*C. commersoni*	BKME (St. Maurice R., QC, Canada)	Histopathology		+		Couillard & Hodson 1996
White sucker	*C. commersoni*	BKME (St. Maurice R., QC, Canada)	Sex steroids, chemical burden		+		Gagnon et al. 1994b
White sucker	*C. commersoni*	BKME (St. Maurice R., QC, Canada)	Growth, reproduction		+		Gagnon et al. 1995
White sucker	*C. commersoni*	St. John R., Canada	Growth, organ size		-		Galloway et al. 2003
White sucker	*C. commersoni*	BKME (Wabigoon R., ON, Canada)	Organ size, reproduction, sex steroids		+		Hewitt et al. 2005
White sucker	*C. commersoni*	BKME (St. Maurice R., QC, Canada)	Chemical body burden, organ size, enzyme biomarkers		+		Hodson et al. 1992
White sucker	*C. commersoni*	Various (Moose R. Basin, ON, Canada)	Ovarian function		-		Janz et al. 2001
White sucker	*C. commersoni*	BKME (Jackfish Bay, ON, Canada)	Sex steroids, enzyme biomarkers, age		+		McMaster et al. 1991
White sucker	*C. commersoni*	BKME (Jackfish Bay, ON, Canada)	Sex steroids, enzyme biomarkers		+		McMaster et al. 1994

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Field Studies (continued)							
White sucker	*C. commersoni*	BKME (Androscoggin R., Maine, USA)	Reproduction, population measures	2 y	-		Mower et al. 2011
White sucker	*C. commersoni*	BKME (Jackfish Bay, ON, Canada)	Sex steroids, organ size, enzyme biomarkers, population measures		+		Munkittrick et al. 1991
White sucker	*C. commersoni*	BKME (Jackfish Bay, ON, Canada)	Sex steroids, enzyme biomarkers		variable		Munkittrick et al. 1992b
White sucker	*C. commersoni*	BKME, BSME (Various, Canada)	Sex steroids, organ size, enzyme biomarkers, dioxin burden		variable		Munkittrick et al. 1994
White sucker	*C. commersoni*	Various (ON, Canada)	Sex steroids, gonad size		variable		Munkittrick et al. 1998
White sucker	*C. commersoni*	BKME (Jackfish Bay/Moose R., ON, Canada)	Stress parameters, enzyme biomarkers	8 y	+		Oakes et al. 2003
White sucker	*C. commersoni*	Various (Wapiti/Athabasca R., AB, Canada)	Enzyme biomarkers, organ size	3 y	+		Oakes et al. 2004
White sucker	*C. commersoni*	BKME (St. Maurice R., QC, Canada)	Enzyme biomarkers, sex steroids, organ size, histology		variable		Parrott et al. 2010
Lake whitefish	*Coregonus clupeaformis*	BKME (Jackfish Bay, ON, Canada)	Enzyme biomarkers, sex steroids, organ size, population measures		+		Munkittrick et al. 1992a
Lake whitefish	*C. clupeaformis*	BKME (Jackfish Bay, ON, Canada)	Enzyme biomarkers, sex steroids		+		Munkittrick et al. 1992b
Lake whitefish	*C. clupeaformis*	BKME (Jackfish Bay, ON, Canada)	Sex steroids, organ size		variable		Munkittrick et al. 1998
Slimy sculpin	*Cottus cognatus*	St. John R., Canada	Growth, organ size		variable		Galloway et al. 2003
Spoonhead sculpin	*Cottus ricei*	BKME (Athabasca R., AB, Canada)	Enzyme biomarkers, organ size		+		Gibbons et al. 1998a
Northern pike	*Esox lucius*	BKME (St. Maurice R., QC, Canada)	Hematology, histopatholgy		variable		Hontela et al. 1997

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Field Studies (continued)							
Tessellated darter	*Ethoestoma olmstedi*	Various (St. Francois R., QC, Canada)	Enzyme biomarkers, sex steroids, fish health		-		Kovacs et al. 2002
Mummichog	*F. heteroclitus*	Neutral sulfite semi chemical pulp mill (Canada)	Organ size, reproduction	21 d	variable		Bosker et al. 2010
Mummichog	*F. heteroclitus*	Various (Miramichi R., NB, Canada)	Immune endpoints		+		Fournier et al. 1998
Mummichog	*F. heteroclitus*	Various (Miramichi R., NB, Canada)	Organ size, reproduction	Sampled weekly for 4 mo	variable		LeBlanc et al. 1997
Eastern mosquitofish	*Gambusia affinis*	Dengcun R. (Sihui, South China)	Morphology, organ size, reproduction		+		Hou et al. 2011
Eastern mosquitofish	*G. affinis*	BKME/UKM (Rice Cr., Florida, USA)	Masculinization	10 y	variable	response eliminated with mill upgrades	Noggle et al. 2010a
Eastern mosquitofish	*G. affinis*	BKME/UKM, Dissolving KME (Rice Cr., Fenholloway R., Florida, USA)	Masculinization, reproduction	2 y	variable		Noggle et al. 2010b
Eastern mosquitofish	*G. affinis*	Fenholloway R., Florida, USA	Morphology, enzyme biomarkers		+		Orlando et al. 2002
Eastern mosquitofish	*G. affinis*	Fenholloway R., Florida, USA	Masculinization		+		Parks et al. 2001
Mosquitofish	*G. holbrooki*	71 locations (USA)	Morphology		+		Bradley et al. 2004
Mosquitofish	*G. holbrooki*	Elevenmile Cr. at Cantonment, Escambia Co., FL, USA	Masculinization, reproductive behavior		+		Howell et al. 1980
Common bully	*Gobiomorphus cotidianus*	Waikato R. (New Zealand)	Ovary pigmentation, recruitment		+		Landman et al. 2008
Common bully	*G. cotidianus*	KME (Tarawera R., New Zealand)	Enzyme biomarkers, organ size		variable		
Blue catfish	*Ictalurus furcatus*	UKME	Enzyme biomarkers, organ size, hematology, histopathology		-		Felder et al. 1998

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Field Studies (continued)							
Redbreast sunfish	*Lepomis auritus*	BKME (Pigeon R., Tennessee, USA)	Enzyme biomarkers, populations measures, community measures		+		Adams et al. 1992
Redbreast sunfish	*L. auritus*	BKME (Pigeon R., Tennessee, USA)	Histopathology		+		Teh et al. 1997
Redbreast sunfish	*L. auritus*	BKME (Pigeon R., Tennessee, USA)	Population measures		+		Theodorakis et al. 2006
Bluegill sunfish	*Lepomis macrochirus*	BKME	Enzyme biomarkers, organ size, immune endpoints, DNA measures	35 d	-		D'Surney et al. 2000
Longear sunfish	*Lepomis megalotis*	Unbleached kraft and recycled pulp mill effluent (Pearl R., Bogalusa, LA, USA)	Masculinization, sex steroids, reproduction	2 y	variable		Fentress et al. 2006
Chub	*Leuciscus cephalus*	BKME (Belgium)	Community measures, population measures, enzyme biomarkers, reproduction measures		variable		Mayon et al. 2006
Tomcod	*Microgadus tomcod*	Various (NB and Nova Scotia (4 mills))	Organ histopathology	3 mo	-		Couillard et al. 1999
Tomcod	*M. tomcod*	Various (Miramichi R., NB, Canada)	Sex steroids, gonad size, reproductive characteristics, enzyme biomarkers	1 y	variable		Williams et al. 1998
Smallmouth bass	*Micropterus dolmieu*	Various (St. Francois R., QC, Canada)	Enzyme biomarkers, morphology		-		Kovacs et al. 2002
Largemouth bass	*M. salmoides*	BKME (St. Johns, Florida, USA)	Sex steroids, organ size, metal and organics burden		variable		Sepúlveda et al. 2002
Largemouth bass	*M. salmoides*	BKME (St. Johns, Florida, USA)	Reproduction success		+		Sepúlveda et al. 2003
Largemouth bass	*M. salmoides*	BKME/UKME (Florida, USA)	Sex steroids, organ size, histology		+		Sepúlveda et al. 2004

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Field Studies (continued)							
Chinook salmon	*Oncorhynchus tshawytscha*	Various (Fraser R., Canada)	Enzyme biomarkers, histopathology, organochlorine burdens		+		Wilson et al. 2000
Eurasian perch	*Perca fluviatilis*	BKME (Norrsundet, Sweden)	Enzyme biomarkers, organ size, hematology, histopathology		+		Andersson et al. 1988
Eurasian perch	*Perca fluviatilis*	BKME (Norrsundet, Sweden)	DNA adducts		+		Ericson & Larsson 2000
Eurasian perch	*P. fluviatilis*	BKME (Lake Saimaa, Finland)	Sex steroids, gonad size, chemical burden, population measures		+		Karels et al. 2001
Eurasian perch	*P. fluviatilis*	BKME (Norrsundet, Sweden)	Community measures, gonad size, morphology		variable		Sandström 1994
Eurasian perch	*P. fluviatilis*	BKME (Norrsundet, Sweden)	Enzyme biomarkers, growth, gonad size, reproduction viability		variable		Sandström 2003
Eurasian perch	*P. fluviatilis*	BKME (Gulf of Bothnia, Sweden)	Community measures, fish health	3 y	+		Sodergren et al. 1988
Eurasian perch	*P. fluviatilis*	BKME (Baltic Sea, Sweden)	Enzyme biomarkers, gonad size, hematology		+		Balk et al. 1993
Eurasian perch	*P. fluviatilis*	BKME (Baltic Sea, Sweden)	Enzyme biomarkers, gonad size, hematology		+		Förlin et al. 1995
Eurasian perch	*P. fluviatilis*	BKME (Lake Saimaa, Finland)	Enzyme biomarkers, sex steroids, chemical burden		+		Karels & Oikari 2000
Eurasian perch	*P. fluviatilis*	BKME (Lake Saimaa, Finland)	Sex steroids, organ size		+		Karels et al. 1998
Carmelita	*Percilia gillissi*	Central Chile	Sex steroids, enzyme biomarkers, population measures	3 seasons	variable		Chiang et al. 2011
Trout perch	*Percopsis omiscomaycas*	Various (Moose R. Basin, ON, Canada)	Enzyme biomarkers, population measures		variable		Gibbons et al. 1998b

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Field Studies (continued)							
Winter flounder	*Pleuronectes americanus*	TMP and sulfite-pulping (Newfoundland, Canada)	Organ size, histopathology	8-26 w	+		Khan & Hooper 2000
Winter flounder	*P. americanus*	TMP and sulfite-pulping (Port Harmon, Birchy Cove, Newfoundland, Canada)	Enzyme biomarkers		+		Khan & Payne 2002
Mountain whitefish	*Prosopium williamsoni*	BKME (Wapiti/Smokey R., AB, Canada)	Enzyme biomarkers		+		Kloeppersams et al. 1994
Mountain whitefish	*P. williamsoni*	BKME (Wapiti/Smokey R., AB, Canada)	Population measures		-		Swanson et al. 1994
Roach	*Rutilus rutilus*	BKME (Lake Vatia, Finland)	Hematology	3 w	+		Jeney et al. 1996
Roach	*R. rutilus*	BKME (Lake Saimaa, Finland)	Sex steroids, chemical burden, enzyme biomarkers		+		Karels & Oikari 2000
Roach	*R. rutilus*	BKME (Lake Saimaa, Finland)	Sex steroids, enzyme biomarkers		variable		Karels et al. 1998
Roach	*R. rutilus*	BKME (Lake Saimaa, Finland)	Sex steroids, chemical burden, enzyme biomarkers, gonad size, population measures		variable		Karels et al. 2001
Lake trout	*Salvelinus namaycush*	BKME (Jackfish Bay, ON, Canada)	Enzyme biomarkers, sex steroids		variable		Munkittrick et al. 1992b
Walleye	*Sander vitreus vitreus*	BKME (Wabigoon R., Dryden, ON)	Sex steroids, gonad size		+		Parks et al. 2001
Catfish	*Trichomycterus areolatus*	Central Chile	Enzyme biomarkers, sex steroids, population measures	3 seasons	variable		Chiang et al. 2011
Eelpout	*Zoarces vivparous*	BKME (Sweden)	Embryonic sex ratios	4 y	variable		Larsson & Förlin 2002
Eelpout	*Z. vivparous*	BKME (Mönsteras, Sweden)	Embryonic sex ratios		+		Larsson et al. 2000a
Eelpout	*Z. vivparous*	BKME (Sweden)	Embryonic sex ratios		+		Larsson et al. 2000b

Common Name	Species name	Effluent Type (Location)	Endpoints	Duration	Exposure Response	Concentration	Reference
Field Studies (continued)							
Various		BKME (Codorus Cr., PA; Leaf R., MS; Willamette R., OR), UKME (McKenzie R., OR)	Community structure, structure and function metrics	10 y	variable	most endpoints unchaged with effluent exposure	Flinders et al. 2009
Various		KME (Elevenmile Cr., Cantonment, FL, USA)	Community measures		variable		Greenfield & Bart 2005
Various		Canada	EEM endpoints		variable		Lowell et al. 2005
Various		Canada	EEM endpoints		variable		Martel et al. 2010
Various		Northern R. Basins, Canada	EEM endpoints		+		McMaster et al. 2005
Various		Canada	EEM endpoints		variable		Tessier et al. 2009

Table adapted from Hewitt (2008) and Dubé et al. (2008). BMKE = bleached kraft mill effluent; BSME = bleached sulfate mill effluent; KME = kraft mill effluent; MP = multiprocess mill (both chemical and mechanical pulping); TMP = thermomechanical mill effluent; UKME = unbleached kraft mill effluent

Response definitions:+ = response observed in all measured endpoints, - = no response seen in measured enpoints, variable= response observed only in some measured endpoints

Abbreviation	Full Text
EROD activity	7-ethoxyresorufin-O-deethylase activity erthrocytic nuclear abnormalities (ENAs)
ENA	erthrocytic nuclear abnormality
11-KT	11-ketotestosterone
E2	17 β-estradiol
GSI	Gonad Somatic Index
HSI	Hepatosomatic Index
CYP1A	Cytochrome P450 (CYP1A)
EMN	erythrocytic micronuclei
MFO	Mixed Function Oxygenase induction

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