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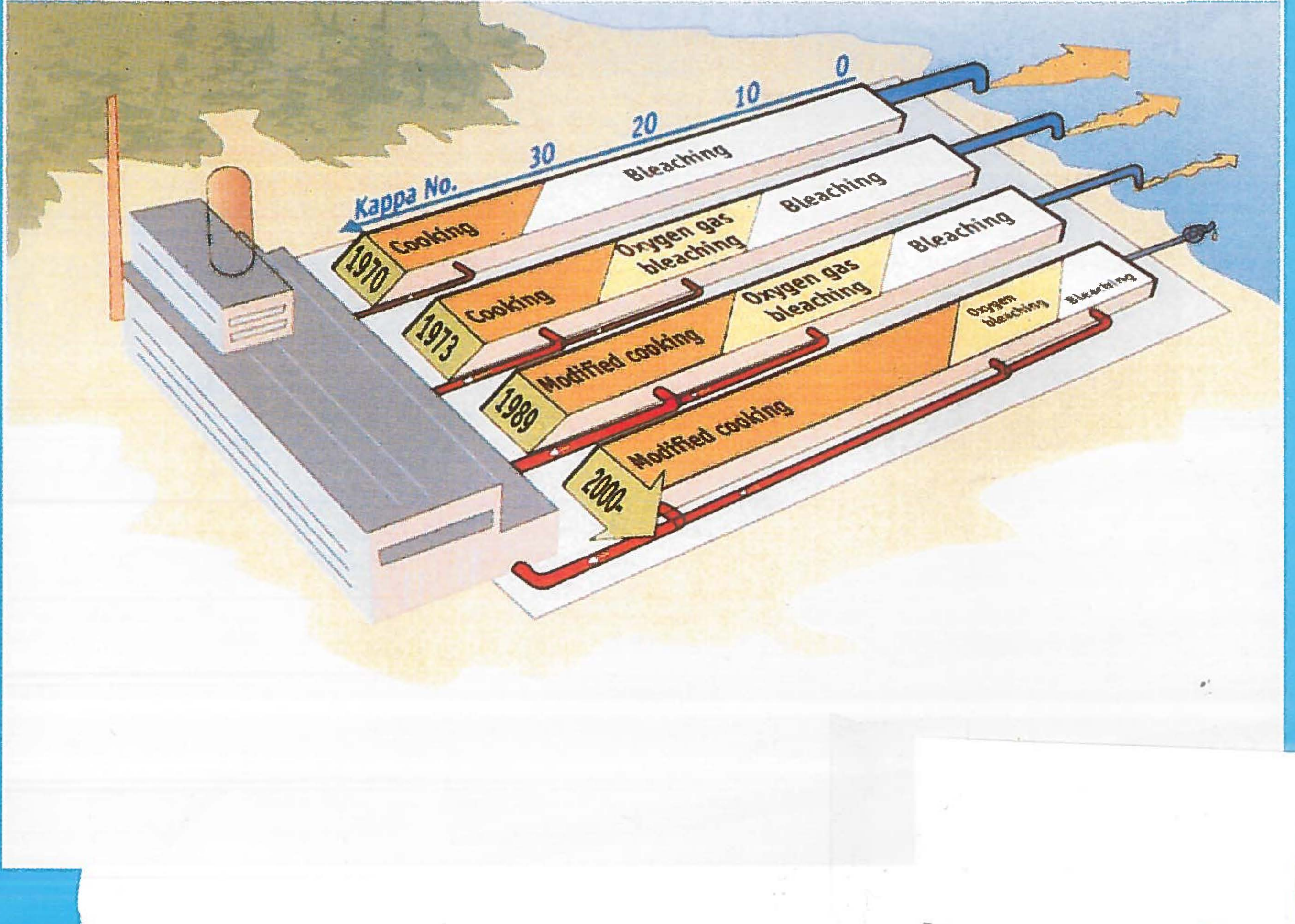
ENVIRONMENTAL PROTECTION

Jukka Tana and Karl-Johan Lehtinen

The aquatic environmental impact of pulping and bleaching operations – an overview



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The aquatic environmental impact of pulping and bleaching operations – an overview

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Introduction

1.1 Objectives

The objective with the present report is to review the recent literature concerning environmental effects of pulp mill effluents in the light of introduction of new bleaching technologies. It is also the aim to see if and how the available scientific material supports the view that bleaching of pulp is responsible for effects noted. Finally, gaps and areas for further research will be discussed. A technical section is included in this review, as the authors assume that also persons without technical background will use this report.

1.2 General background

The development of the pulp and paper industry after World War II resulted in a greatly increased production of bleached pulp of different qualities. According to FAO statistics (FAO 1992), the world paper and paperboard production was about 240 million tons in 1990. Bleached kraft represented about 22 % of the total furnish. Wood pulp was about 56 % of the total furnish, while 44 % was from other sources, including recycled fibre and non-wood fibres. Dominating pulp producers are the industrialized countries of the northern hemisphere, i.e. USA, Canada, Sweden, Japan and Finland. Finland and Sweden, in particular, largely rely upon the revenue from exports of pulp and paper products. This is due to the high "nativeness" of these products, i.e. very little import is needed in order to support the production.

The expansion of pulp production in Finland can be illustrated by data from 1980 (FAO 1987) and 1993 (Association of the Finnish Forest Products Industries). In 1980, the production of bleached kraft pulp (sulphate and sulphite) was 3.1 Mt (million tons). In 1993, the kraft pulp production was 6 Mt. A further national increase is expected during the rest of the 1990s. Internationally the trend is likewise expected to increase and the total increase in paper furnish demand is estimated to be about 90 million ton before year 2010. Recycled fibre is expected to cover over 50 % of the increase.

The pulp and paper industry has historically been considered a major consumer of natural resources, including water, and a significant contributor of pollutant discharges to the environment (Folke 1991). However, pulp and paper mills have the potential of being environmentally friendly industries, working on a sustainable basis (Folke et al. 1991). The raw material is a renewable resource; no external energy is needed (chemical pulp); it is possible to recycle or recover energy from the products, thereby avoiding a solid waste disposal problem.

During the period between 1945 and the 1960–1970s the pulp and paper industry caused substantial waste water discharges into receiving waters. The effects observed were sometimes of dramatic character with oxygen depletion and fish kills. The reasons for such effects were the high discharges of oxygen consuming suspended and dissolved solids, which exhausted the dissolved oxygen available, especially in water bodies with limited effluent dilution capacity. From the end of the 1970s until recently, the main emphasis was put on the role of chlorinated substances formed in the bleach plant. This was due to the fact that some synthetic chlorinated organic substances such as PCB's and DDT have been found to accumulate in the aquatic organisms and cause, for example, impairment of reproduction in organisms at the top of the food web. As a consequence, all chlorinated organic substances were regarded, in the public discussion, as man-made, non-degradable, bioaccumulative and hazardous to biological systems.

For the pulp industry, the public concern, mainly driven by NGOs (non-governmental organizations), about the potential environmental hazard imposed by the use of chlorine in the bleach plants has brought about a drastic decrease in the use of elementary chlorine as a bleaching chemical during the last decade. The environmental control authorities in many countries, including Sweden and Finland have set severe restrictions on the discharges of chlorinated organics measured as AOX (Adsorbable Organic Halogen) into the aquatic environment. In Sweden the Swedish EPA's limit 1.5 kg AOX/t pulp came into effect in 1992 and in Finland the a limit of 1.4 kg AOX/t pulp becomes the official limit in 1995. Several countries have even proposed a complete elimination of AOX-discharges, apparently based on the belief that AOX is solely of anthropogenic origin (Lehtinen 1992). In reality the goal of 1.4 kg AOX/t pulp has already been outdistanced by the industry in Finland and Sweden. The AOX-discharge in Sweden was 0.6 kg/t pulp in 1992 and in Finland in the beginning of 1994 0.4 kg/t pulp (Association of the Finnish Forest Products Industries) (Figure 1).

This was achieved by a combination of several measures: First of all the use of elementary chlorine has been replaced by chlorine dioxide and introduction of other oxygen-containing chemicals such as molecular oxygen, peroxide and ozone. In 1980 the use of elementary chlorine in Finland was about 200 000 tons, whereas the use in 1993 had dropped to about 20 000 tons. At the same time the consumption of chlorine dioxide increased from 60 000 tons in 1980 to about 150 000 tons in 1993. Oxygen as bleaching medium had increased from zero to about 50 000 tons during the same time period. Another contributing factor to the decreased emissions of AOX into Finnish receiving waters is the installation of external treatment plants of different designs. In 1994, 26 forest industrial sites had activated sludge treatment plants, four had aerated lagoons and two sites had anaerobic effluent treatment in operation. Finally, most mills have decreased their waste water emissions by increased closure of the processess, improved spill control, sewer design, handling of condensates and improved process control (Owens & Lehtinen, 1995 in press). The waste water discharges within the Finnish forest industry decreased nearly 2/3 from 1 800 000 m^3/yr in 1973 to 650 000 m^3/yr in 1993.

In order to comply with market and environmental demands the current trends within the pulp and paper industry, at least in Scandinavia and Canada, is towards increased closure of the bleach plants either by using ECF (Elementary Chlorine Free) or TCF (Totally Chlorine Free) bleaching of the pulp.

Whereas the environmental impacts of ECF pulp bleaching, as well as other bleaching technologies, have been extensively investigated, comparably little is published about TCF pulp bleaching in the open literature (Kovacs et al. 1995). The development of TCF pulp bleaching technologies was brought about more by NGO-driven concerns than scientific evidence regarding the potential effects of the chlorinated substances formed in the bleach plants in the 1980s. In Sweden, the rapid transformation of the pulp bleaching process technology during the last decade was, in fact, mainly driven by a series of scientific rebounds, such as over-interpretation and, in some cases, misinterpretation of the scientific material re-

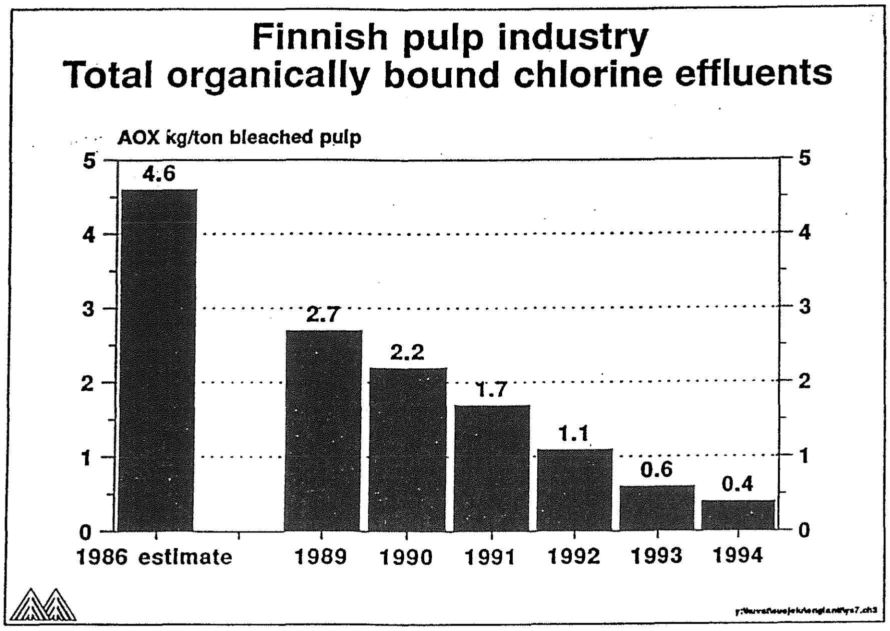


Figure 1. Total organically bound chlorine load expressed as AOX from Finnish pulp industry between 1986–1994.

garding environmental impacts (Landner et al. 1994a). The most prominent steps in this series of events, which mostly was promoted by suspicions and concern rather than by scientific evidence, were pointed out by Landner et al. (1994a) according to the following:

• The most dramatic environmental damage hitherto demonstrated in a pulp mill effluent receiving water was the disappearance of the bladder-wrack community within a 12 km² area outside the Mönsterås pulp mill in the 1980s (Lindvall & Alm, 1983). By a series of mainly mesocosm experiments, it was shown that the most important reason for the damage was an inorganic chlorinated substance, i.e. chlorate (Rosemarin et al. 1986; 1994; Lehtinen et al. 1988). The increased disharges of chlorate in their turn were due to the introduction of improved environmental technology, namely partial exchange of elementary chlorine for chlorine dioxide.

• The occurrence of biological effects in pulp mill effluent receiving waters was established through a series of observations on malformed fish, and later, physiological changes as well as reproduction disturbances in fish (Andersson et al. 1988; Sandström et al. 1988). Consequently, it was unequivocally shown that biological effects occurred in waters receiving effluents from bleached kraft mills using chlorine bleaching. However, no attempts to distinctly connect observed effects to exposure to one or several chlorinated organic compounds were made. Furthermore, it was later shown that the most thoroughly studied effluent receiving area during the period of investigation (1984-1985) was also exposed to high discharges of black liquor, washing losses and residual acid as well as contaminated sludges. These events make a connection between cause and effects extremely uncertain.

• The stringent demands on reduced AOX-emissions from the Swedish pulp industry may therefore be considered to have been set by "precautionary reasons" and not as a consequence of scientifically established damage caused by chlorinated organic substances occurring in receiving waters. This condition was also pointed out by Södergren (1988) in the summary from the Swedish EPA project

"Environment-Cellulose I": Despite the fact that no specific chlorinated organic compounds were possible to relate with observed effects in the receiving water, their mere presence are a matter of concern, above all considering what is previously known about chlorinated compounds with similar properties. That this chlorinated material might reach a large scale distribution is as well unacceptable, since in such case a reduction or remediation of possible damage would be impossible".

• Thus, it may be concluded that the possibly largest industrial process restructuring performed in a short time within the Swedish industry – and followed by the Finnish and Northamerican industry – largely was done on the basis of unproven suspicions. Furthermore, recent investigations have shown that some of the effects observed in fish, that previously were connected to chlorinated compounds, as a matter of fact, can be produced at exposure to other, non-chlorinated compounds present in pulp mill effluents (Lindström-Seppä et al. 1992a; O'Connor et al. 1993; Lehtinen et al. 1993). Nevertheless, the elimination of chlorine as a bleach chemical in the pulp industry has brought about a positive environmental effect. This is mainly due to the strong reduction of the chloride content of the effluents, which has allowed a closure of the mill system and recycling of the bleach plant effluent back to chemical recovery system of the mill. Thereby, also the unchlorinated toxic compounds can be withdrawn from the discharges to the environment.

Technical development and environmental implications

2

Pulp is produced by several methods (Solomon et al. 1993; McCubbin 1983; Dellinger 1980; Casey 1980; Beeland et al. 1979). These production techniques yield different products and by-products and are usually grouped into mechanical and chemical (sulphite and kraft) pulping. Mechanical pulping involves conversion of wood into fibres by physical or mechanical grinding, aided in some cases by heat, high pressure and/or chemicals. Cellulose and lignin may also be separated by chemical methods where lignin is depolymerizing and dissolved. Chemical pulping is conducted by two processes, the sulphite process and the kraft (sulphate) process. The latter process dominates the industry because it more easily allows recovery of valuable chemicals and, as a result, minimizes discharges into the environment (Solomon et al. 1993; Kleppe 1970). Bleached kraft and thermomechanical pulp are the grades that have been responsible for the recent growth of the wood pulp supply (Figure 2).

In spite of environmental pressures and as a result of the major progress made so far, the dominance of bleached kraft is predicted to continue (Folke et al. 1993a). In the following discussion attention will mainly be paid to the bleached kraft process.

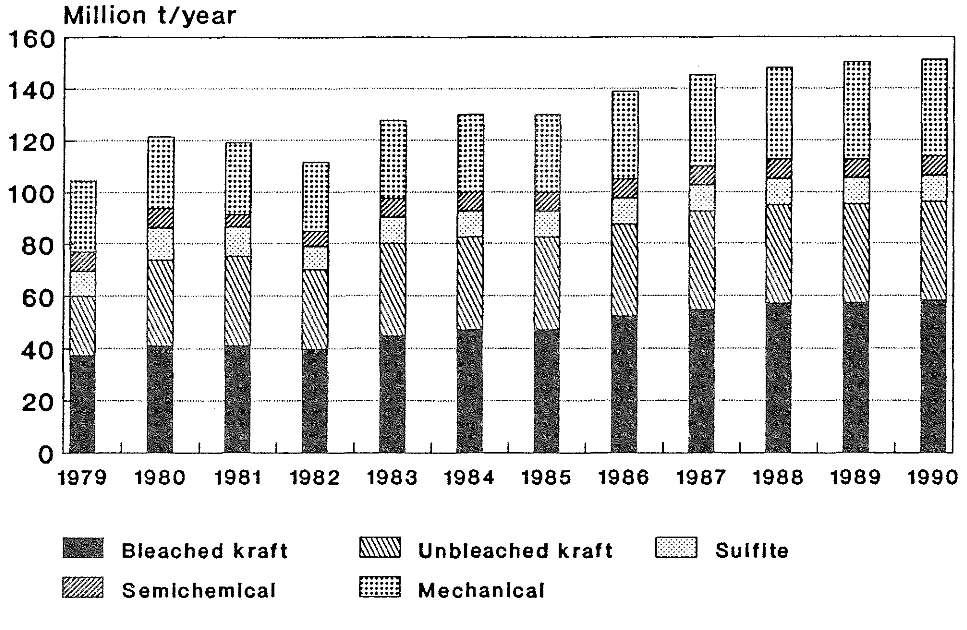


Figure 2. Development of wood pulp supply (Source: FAO, 1992 and Folke et al. 1993a).

2.1 Main features of conventional kraft pulping

2.1.1 The pulping process

The pulping process removes the lignin from the wood fibres by dissolving it in the cooking chemical solution (white liquor), thus uncovering the fibres. The lignin cannot be completely removed without harming the fibre material. The amount of residual lignin, or the delignification degree, is measured by the Kappa No. A high Kappa No. indicates high residual lignin in the pulp. This lignin has to be removed in the bleaching process. The higher the Kappa No., the higher the use of bleaching chemicals.

From the 1950s onwards, some pulp mills changed from batch cooking to the continuous cooking method. This is done in a tall digester vessel where heated white liquor and wood chips flow countercurrently until the delignification is achieved at about the middle of the digester. The rest of the digester is used as a Hi-heat wash zone with counter current fibre/liquor flow (Folke et al. 1993a).

The kraft process can utilize wood raw material from many different sources. The quality of wood has, however, a great influence on the properties of the end product. The quality of the finished pulp is the main criterion to determine the pulping conditions. The strength and Kappa No. of the pulp largely determine the provisions for high quality and clean pulp. The Kappa No. of the unbleached pulp will also influence the quality of the bleach plant effluent. A high Kappa No. to the bleach plant is closely related to the amount of AOX formed and the chemical charge (Annergren et al. 1987; Axegård 1989; Berry et al. 1991; Reeve & Earl 1989).

2.1.2 Brown stock washing

Washing of the cooked pulp is done with water to remove the dissolved organic material and the residual chemicals from the pulp. A continuous digester plant utilizes the Hi-heat wash zone in the digester plus drum washers or diffuser washers. Older mills often feature fairly high washing losses to the sewer from an open screening room. Washing results are largely determined by the efficiency of the equipment used and the amount of water applied. The washing results are improved as the wash water amount is increased. However, the evaporation demand will be increased.

The dry solids lost to the sewer in the unbleached area has a significant impact on the brown stock area effluent discharges. Typically the black liquor dry solids lossess correspond to 0.3 kg BOD_7/kg ds. and 1.1 kg COD/kg ds. (Folke et al. 1993a).

The black liquor carryover to the bleach plant impacts the bleach plant chemicals consumption and the bleach plant effluent quality.

2.1.3 Pulp bleaching

The purpose of bleaching is to remove the residual lignin from the unbleached pulp and to make the pulp more white and bright according to the quality specifications.

Several bleaching chemicals are being used in the industry. The common bleaching chemicals together with their letter symbols in the bleaching sequence are:

Symbol	Chemical	Symbol	Chemical
C	Chlorine	Z (O_3)	Ozone
D	Chlorine dioxide	E	Sodium hydroxide
H	Hypochlorite	X	Enzymes
O	Oxygen	Q	Chelating agents
P	Hydrogen peroxide	A	Acid

Source: Folke et al. 1993a

Different chemicals react with the pulp lignin in different ways. The chemicals can be divided into three groups (Folke et al. 1993a, Poppius-Levlin 1992):

I Cl_2, O_3 and H_2O_2 (under acid conditions)
- react with all aromatic lignin units
- electrophilic reaction

II O_2 and ClO_2
- react mainly with units possessing free phenolic hydroxy groups,
- electrophilic reaction

III H_2O_2 (under alcaline conditions) and NaOCl
- react mainly with carbonyl groups in lignin
- nucleophilic reaction

Bleaching is carried out as a continuous process by alternating between delignifying stages (using any of OCDHPZ) and dissolved material extracting stages (E). Sometimes the extraction may be combined with delignification (O and/or P).

A conventional bleach plant may feature five or six stages such as the sequences (CD)EDED or (CD)EHDED. The latter sequence is today being used in North America to some extent, while in Scandinavia (and in many mills in North America, too) the hypochlorite has been essentially abandoned. Letters in brackets indicate that several chemicals are used in the same stage. It became a common practice in 1980s to substitute part of the chlorine with chlorine dioxide in the first bleaching stage. The amount of chlorine replaced is referred to as the degree of chlorine dioxide substitution. Today chlorine gas is practically completely replaced with chlorine dioxide in Scandinavia.

Another important parameter that is necessary to understand is the active chlorine, which refers to the amount of chlorine or other compounds that are applied given as equivalent chlorine used in the bleaching.

The active chlorine equivalents are:

- for chlorine 1 kg active chlorine/kg Cl_2
- for chlorine dioxide 2.63 kg active chlorine/kg ClO_2
- for hypochlorite 0.95 kg active chlorine/kg NaClO

Figure 3 illustrates the fibre line of what may be considered as a "conventional" bleached kraft pulp mill. There is a small amount (30 % of active chlorine) of ClO_2 added to the chlorination stage, i.e. the ClO_2 substitution degree is 30 %.

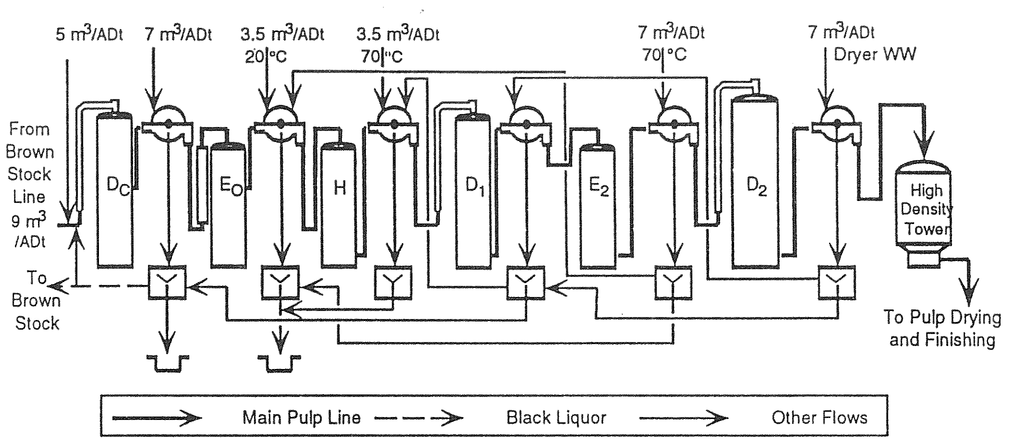


Figure 3. Conventional bleach plant flowsheat. (Source: Duoplan Oy in Folke et al. 1993a).

2.2 Replacement of chlorine with chlorine dioxide – discharge benefits

The driving force within the pulp industry for increased substitution of chlorine with chlorine dioxide, as well as an increased use of other oxidative chemicals (peroxide, ozone and oxygen), is external demands on decreased emissions of mainly chlorinated organics (Lehtinen 1992). In order to understand the incentive for an increased use of chlorine dioxide instead for chlorine, the differences in the fundamental chemistry of these two chemicals in the bleaching need to be described. Bleaching with chlorine-containing agents involves the chlorine atom at different oxidation levels (Solomon et al. 1993). Table 1 shows various inorganic chemical species involved in bleaching and the oxidation level of the chlorine atom in each species.

Table 1. Inorganic chlorine species involved in bleaching (Scource: Solomon et al. 1993)

Chemical species	Formula	Oxidation level of chlorine atom
Chlorate ion	ClO^{3-}	+5
Chlorine dioxide	ClO_2	+4
Chlorite ion	ClO^{2-}	+3
Hypochlorite ion	ClO^-	+1
Hypochlorous acid	HOCl	+1
Chlorine	Cl_2	0
Chloride ion	Cl^-	–1

The oxidation level of the chlorine atom in chlorine dioxide is +4, while in molecular chlorine the oxidation level of the chlorine atom is 0. Based on reduction to chloride ion which has an oxidation level of –1, there is a change of five oxidation levels in the case of chlorine dioxide and one oxidation levels in the case of molecular chlorine. Thus, chlorine dioxide is a much stronger oxidant than chlorine. Since bleaching is essentially the oxidation of lignin, chlorine dioxide is therefore more effective for removing lignin from pulp by oxidation.

Chlorine (Cl_2), in addition to acting as an oxidizing agent, also acts as a chlorinating agent. In the chlorination process, an organic molecule RH reacts with chlorine to give a chlorinated organic substance RCl and HCl:

$$RH + Cl_2 \quad RCl + H^+ + Cl^-$$

In some cases, the group R is aromatic, resulting in a chlorinated aromatic compound. In the first bleaching stage, about half the chlorine applied to pulp combines with the lignin and the remainder oxidizes the lignin and is converted to chloride ion (Hardell & de Sousa 1977; Kempf & Denke 1970).

Chlorine dioxide reacts differently with lignin. Radical mechanisms oxidize the lignin to muconic acid esters, thus breaking aromatic structures in the lignin. However, chlorinated derivatives may also be produced. Chlorine dioxide is normally considered to have 2.5 times the oxidative power of Cl_2 on a mole to mole basis (see active chlorine equivalents above). This is correct in a case where the total oxidation capacity of the compounds is effectively expressed. Sometimes small amounts of chlorine may be produced from the chlorate precursor, particularly with older chlorine dioxide generators (Kolar et al. 1983; Ljungren et al. 1992).

A number of investigators have examined the impact of increased substitution of chlorine for chlorine dioxide on bleach plant effluents. Their studies show that substantial substitution of chlorine with chlorine dioxide reduces effluent colour, BOD, COD, chlorinated organics, and toxicity (Hardell & deSousa 1977; Donnini 1982; Donnini 1983; Axegård 1989; Annergren et al. 1987; Bryant & Amy 1988; Gergov et al. 1988). A few years ago a higher degree of substitution was considered to adversely affect the economy and quality of pulp. Today, the use of 100% chlorine dioxide is possible, if part of the delignification needed for full pulp brightness is transferred from the D-stage to the following extraction stages and these are enforced by oxygen and peroxide (McCubbin et al. 1992). Formation of chlorinated phenolics is known to increase when chlorine dioxide substitutes chlorine in the range of about 20–50% substitution (du Manoir & Dubelsten 1989) (Figure 4). Still higher substitution lowers the formation of chlorinated phenolics (Dahlman et al. 1993a; O'Connor et al. 1993).

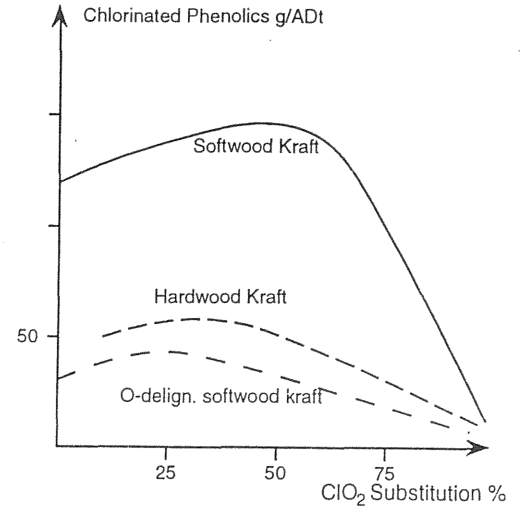
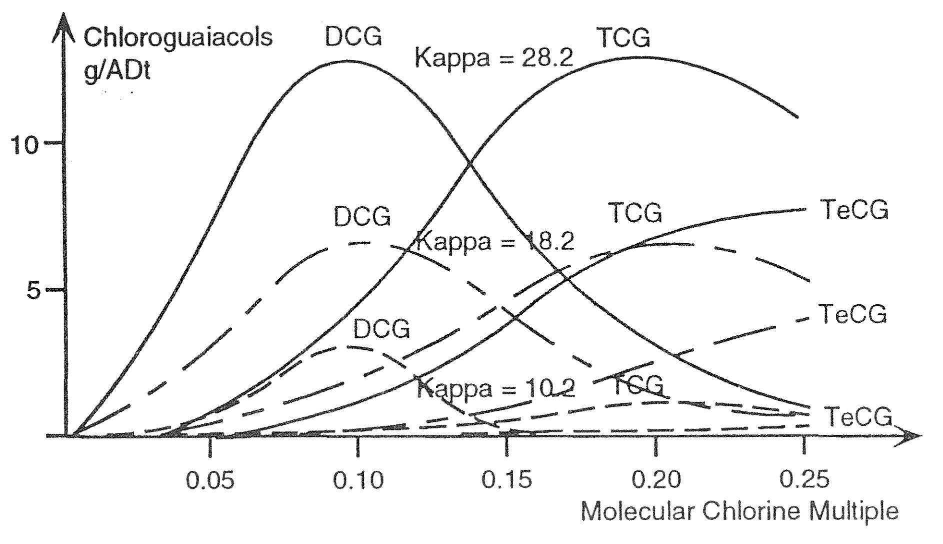


Figure 4. Change in formation of chlorophenolics as a result of chlorine substitution for chlorine dioxide. (Source: Folke et al. 1993a orig. du Manoir & Dubelsten 1989).

The organic material in the effluents from mills producing bleached pulp is composed of a very complex mixture of substances varying in chemical structure and molecular weight (Axegård et al. 1993). These substances originate mainly from the wood raw material: polysaccharides, lignin and extractives. The amount of organic material in a total pulp mill effluent depends to a large degree on the Kappa No. of the pulp entering the bleach plant, but also on unit operations in other parts of the mill (wood debarking, brown-stock washing liquor, condensates). Different brownstock kappa No.s together with the chlorine multiple have also an influence on the amounts and degree of chlorination of chloroguaiacols (Figure 5). The lower the chlorine multiple the lower formation of highly chlorinated phenolic compounds.

Since the middle of the 1980s it has been known that chlorine-based pulp bleaching involves formation of polychlorinated dioxins (PCDDs) and furans (PCDFs). During the late 1980s, the production of PCDDs/PCDFs was found to be a result of contamination of the pulping liquors with dibenzo-p-dioxin and dibenzofurans that subsequently reacted with chlorine in the bleaching stages (Voss et al. 1988).

Although chemicals that can be converted into chlorinated dioxins and furans are widely distributed in the environment, the major source of precursors was identified as defoamers made from oils with high aromatic content (Berry et al. 1991). Substitution of chlorine for chlorine dioxide, improved brown stock washing, reduced Cl_2-factor and stepwise chlorine addition practically totally eliminated the formation of PCDDs and PCDFs in pulp bleaching plants as shown in Figure 6.



Kappa No 28.2
Kappa No 18.2
Kappa No 10.2

Figure 5. Formation of chloroguaiacols vs. molecular chlorine multiple for different Kappa No.s (Source: Folke et al. 1993a). DCG = dichloroguaiacol; TCG = trichloroguaiacol; TeCG = tetrachloroguaiacol.

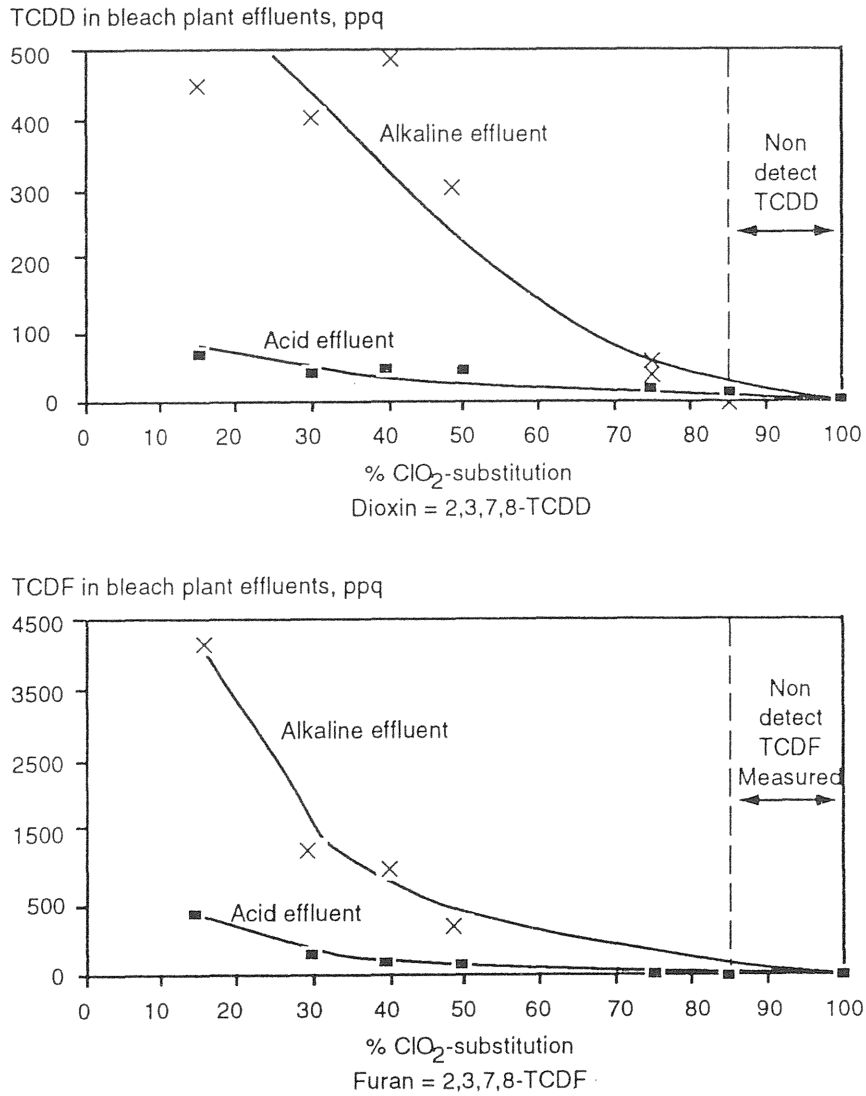


Figure 6. Effects of chlorine dioxide substitution on TCDD/TCDF levels in bleach plant effluents.(Source: Folke et al. 1993a).

The substitution of chlorine gas for chlorine dioxide and other bleaching chemicals in modern processes have decreased the discharges of AOX and organic material measured as COD considerably (Table 2). High AOX values, up to 7 kg/t pulp, used to originate from old kraft mills with high chlorine use in the first bleaching stage and without oxygen delignification. AOX loads ranging from 0.1–1.0 kg/t pulp have been reported for kraft mills using chlorine dioxide but no chlorine in the bleaching process (Brunsvik et al. 1989, 1991). The variation depends on differences in cooking, bleaching and effluent treatment technology. Important measures to reach low AOX levels (below 0.2 kg/t pulp) are extended cooking, oxygen delignification, low chlorine multiple bleaching (< 0.15), elimination of chlorine gas as a bleaching chemical and secondary effluent treatment (Axegård et al. 1993).

Table 2. Typical discharges of COD and AOX from various standard processes for production of bleached softwood kraft pulp of ISO-brightness 88-90%. AL= aerated lagoon, AS=activated sludge treatment. (Source: Axegård et al.1993).

Year	Process	COD kg/tp	AOX kg/tp
1970	CEHDED	100	7
1980	O(C90+D10)EDED	55	3
1990	O(D50+C50)(EO)D(EP)D + AL or AS	45	1.5–2.0
1993	Modified cook OD(EOP)D(EP)D OQP, OQPZP, OAZQP + AL or AS	25	< 0.2

2.3 Totally chlorine free bleaching, TCF

Due to market demands for products bleached without use of chlorine compounds (TCF-techniques), considerable research efforts have recently been directed to find methods to replace chlorine dioxide as well (Axegård et al. 1993). The main TCF-chemicals used are hydrogen peroxide and ozone. Prolonged selective delignification down to Kappa numbers of about 10 for softwood kraft pulps has facilitated the use of these chemicals.

Hardwood kraft pulps can be bleached to full brightness, and several mills use this technique. Sofar, 85–88% ISO-brightness has been obtained in full-scale production (Axegård et al. 1993). It is technically feasible to recycle most effluents from TCF bleaching to the recovery system, where it is reasonably safe to assume that all organics will be effectively destroyed. However, the mills practicing TCF pulp bleaching have not generally recycled these effluents, although they report a long term objective of doing so (Folke & Renberg 1994).

The rapidity of acceptance of ultra-low chlorine and TCF pulp bleaching in Scandinavia, without recovery of bleach plant effluents, to accomodate customer and regulatory demands to eliminate AOX discharges, demonstrate the weakness of a zero AOX regulation. The TCF operations in Scandinavia have probably eliminated AOX discharges, with little or no environmental benefit relative to prior operations, and may even be discharging effluent which is more toxic than that from a modern bleach plant with high chlorine dioxide substitution and extended cooking or oxygen delignification (Folke & Renberg 1994; Kovacs et al. 1995).

TCF sequences involving peroxide necessarily lead to the discharge of EDTA, DTPA or similar metal chelating agents. According to Walterson & Landner (1993) it may be concluded that the various results show that free EDTA and metal complexes of EDTA are susceptible to biodegradation under aerobic conditions. Although the rate of biodegradation is too slow to ensure efficient removal during biological treatment of sewage (high content of amino acids and sugars may play an important role), EDTA and its complexes will not persist indefinitely in receiving waters and soils. More information is, however, needed to estimate the extent of EDTA's partitioning to sediments as well as the extent and role of bio-/photodegradetion under environmental conditions. The use of different chelating agents in the Finnish pulp and paper industry is presented in Table 3.

Table 3. The use of different chelating agents, t/a, in the Finnish pulp and paper industry in 1994. (Source: Finnish Environment Agency, 1994).

	EDTA	DTPA	Others
Bleached kraft pulp	884.5	2 080.0	0
Bleached mechanical pulp	1 978.5	2 189.1	60
Deinking	0	285.0	58.2
Other use	32.5	0	0
TOTAL	2 895.5	4 554.1	118.2

2.4 Indreased mill closure

It is often stated that TCF pulping is on the track to be the closed cycle bleach plant (Pulp & Paper Canada, Report 1993). Several authors have suggested that ECF pulping can achieve the same (Strömqvist 1994). In both cases, non-process elements brought in with the wood are dissolved from the pulp. These elements include silica, aluminium, manganese and potassium each of which must be balanced by installation of additional "kidney" functions. The spent bleach liquor cannot just be recycled to the recovery system. For ECF pulp, an additional chloride "kidney" must be installed.

Chloride removal is a major problem, and the only full-scale closed process yet installed (Thunder Bay, Ontario, in the 1970s) has failed, despite considerable research and investment. However, modern ECF bleach sequences such as the relatively widely used ODEoDED discharge only about 20% of the chloride common in the traditional CEDED and similar bleach sequences (Folke & Renberg 1994). Once the chloride is removed, the ECF mill is facing the same problems with trace metals, scaling and maintaining the hydraulic balance in day to day operations as a TCF mill attempting to operate with a similar degree of closure of the water system. At present, both ECF and TCF appear to be viable routes towards substantial reduction of the environmental effects of mills. The degree of recovery achieved of the organic substances will be more important than the bleaching sequence used (Folke & Renberg 1994).

2.5 External treatment

Biological treatment is the dominating external treatment method for pulp mill effluents. The methods used are almost exclusively either activated sludge or aerated lagoon type installations. Some sulphite mills and mechanical pulp mills use anaerobic treatment methods. Chemical treatment is applied in some mills after the biological treatment of effluents mostly for color removal.

In the aerated lagoon, the effluent is aerated for several, up to 12–15 days. The concentration of micro-organism is low, which means that a long reaction time is needed. Prior to the lagoons the effluent is typically clarified and neutralized to a pH suitable for the micro-organisms. The lagoon is aerated usually by surface aerators although submerged aerators with central air blowing system have been used in some cases.

In an activated sludge treatment system the biosolids' concentration in the aeration pond is maintained high by recycling the biosludge to the feed. The system typically consits of a primary clarifier, an aeration basin (reactor) and a secondary clarifier. Effluent pretreatment normally includes a neutralization system, a nutrient control and in some cases a process effluent cooling system. Biologically active sludge is separated from the aerated effluent in a secondary clarifier. Most of the biological mass is returned to the feed and combined with process effluent. The excess sludge is taken to the sludge thickener and pressed combined with the primary sludge. The pressed sludge is disposed either by incineration or landfill.

Methodologies applied at pulp mill effluent impact assessments

3

An assessment of the environmental hazard of substances contained in pulp mill effluents normally involves three different exercises, i.e. exposure, effect and ecosystem analyses (OECD, 1982; Landner 1988; Landner 1989). Exposure analysis involves the identification and analysis of contaminants, and a determination of the environmental fate of substances. Effect analysis is concerned with toxic effects of chemicals and physical agents on living organisms, especially on populations and communities within defined ecosystems. It includes the identification and determination of acute and chronic environmental toxicity and all effects on living species such as mortality, fecundity, histopathological effects, enzymatic changes, and other physiological effects (Folke et al. 1993a).

Chemical and physical characterization of pulp mill effluents is involved in the exposure analysis. This field is discussed in section 4. The effect analysis is made in section 5. In this section, the methodologies applied at the effect analysis, are discussed.

Biological characterization is the relevant measure to define the occurrence and extent of environmental impacts on aquatic organisms (Owens & Lehtinen, 1995 in press). The biological characterization can be divided into four organizational levels: community, population, whole-organism measurements, and within-organism measurements. A community is the close interaction of species such as: a) organisms living on or in the bottom sediment, the benthic community, or b) the near shore areas of water bodies, the littoral community. A population is the group of individuals from a single species which inhabit the site. Communities and populations are the biological measurements where adverse effects are considered meaningful and to require remediation. The third and the fourth organizational levels are, respectively, a) whole-organism or individual measurements such as weight and length and b) within-organism measurements (where further subdivisions are: organ, tissue, cellular, subcellular, and molecular).

Certain changes at these lower organizational levels are not fatal and are referred to as sub-lethal. The use and interpretation of many whole-and within-organism endpoints (biomarkers) are currently the subject of intense study and debate among ecotoxicologists. These endpoints may or may not be connected with meaningful changes at higher levels of organization, so their relevance and meaning are currently uncertain.

3.1 Single-species tests

A toxicity test in laboratory uses a uniform population of a selected species, a series of effluent concentrations, a set time, and then measures a relevant endpoint such as mortality, growth or reproduction. The end result is the median concentration which is lethal to 50% of the test population (LC50) or where a biological response reaches half of its maximum intensity (EC50). The inhibition concentration (IC25) is a more sensitive endpoint, where a response reaches 25% of the maximum (Owens & Lehtinen, in press; McLeay 1987).

By definition, acute toxic effects are those which occur within a relatively short period of time (usually between 48 or 96 h). These effects may be lethal (death within short-term exposure) or sublethal, depending on the strength of the toxicant and on the tolerance of the test organism. It is noteworthy that the literature often and also incorrectly equates the term "acutely toxic" with acutely *lethal*, ignoring acute sublethal toxic effects (McLeay, 1987).

Both the Scandinavian and North American countries have developed and promulgated as regulatory tools single-species, mostly freshwater, toxicity tests using fish (fathead minnow, *Pimephales promelas*, rainbow trout, *Oncorhynchus mykiss*, zebra fish, *Brachydanio rerio*), water flea, (*Daphnia magna* or *Ceriodaphnia dubia*), green alga, (*Selenastrum capricornutum*),luminescent bacteria (*Vibrio fisheri*), to mention the most commmonly used tests. Single-species tests omit several exposure routes for toxic substances (food sources, sediment contact and ingestion, and potential environmental transformation of effluent components) and critical endpoints such as fish reproduction.

3.1.1 Acute and short-term bioassays with fish

Laboratory methods for measuring the acute lethal toxicity of effluents to fish have been established and have been in common use since the 1950s. Specific procedural details for conducting these laboratory bioassays have been published (Nordforsk 1982; OECD 1981; Sprague 1969) and national and international standards for acute toxicity test are published in ISO- and SFS-catalogues (ISO 1995, SFS 1994).

Rainbow trout is routinely used as a test fish in Scandinavia, Canada and northern U.S. states where waters receiving pulp mill effluents are cool. In warmer climates, warmwater fish species (i.e. fathead minnows, golden shiners, *Notemigonus crysoleucas*, bluegill sunfish, *Lepomis macrochirus*) are employed.

The LC50 bioassay involves placing groups of fish (usually ten per concentration) in a range of concentrations of effluent, diluted with freshwater (to which the fish are acclimated), and observing their survival throughout a 96-h test period. Based on the percentage survival of fish at various effluent concentrations, the median lethal concentration is calculated. Since effluent dilutions are normally on a volume-to-volume basis LC50 values are expressed as percentage effluent (% v/v). The higher the LC50 value, the less its toxicity, i.e. the higher the concentration the fish or other aquatic organism can tolerate. Samples of effluent identified as "non-toxic" are those in which more than half (50%) of the test fish exposed to full-strength effluent for 96-h survived (McLeay 1987).

A number of test variables, controlled or uncontrolled, can influence (often markedly) LC50 values. For instance, untreated or clarified pulp mill effluent samples appear to be from two to four times more toxic if test solutions are renewed (semi-static or continuous flow tests) during the bioassay (Loch and MacLeod 1974; Walden et al. 1975). Inter- and intralaboratory LC50 or other lethal bioassay results for samples of pulp mill effluents may also differ due to variations in the overall condition and tolerance of fish stocks, differing fish-loading densities and/or aeration rates, and sample pH, etc. (McLeay 1987). The use of replicate (duplicate or triplicate) bioassay tests with the same effluent sample enables an understanding of the validity and reproducibility of the intra-laboratory test results (Sprague and Fogels 1977). However, as a cost-saving measure, bioassays conducted for routine monitoring or even legal purposes are often not replicated.

3.1.2 Toxic Unit concept

"Toxic units" were originally proposed as a method for expressing the toxicity of chemicals or effluents to fish in terms related directly to the concentration of toxicants (Sprague and Ramsey 1965; Sprague 1971). According to this concept, one toxic unit (TU) corresponds to the concentration of chemical(s) or effluent dilution which kills 50% of the test fish within 96 h, i.e. 1 TU = 96-h LC50. Using this approach the "amount of toxicity" in a particular effluent is expressed in terms of toxic units, as follows:

$$TU = \frac{100\%}{\text{96-h LC50 (\%)}}$$

For example, an effluent with a 96-h LC50 value of 20% (v/v) contains 5 TU, whereas a more toxic sample would contain a correspondingly higher number of toxic units (i.e., for a 96-h LC50 of 4%, TU = 100/4 or 25). The advantage of this approach is that toxic values increase directly and linearly with toxicant concentration, known or otherwise, whereas this is not so for other bioassay values (McLeay 1987).

The toxic unit concept is useful to assess the quantity of toxicity discharged daily by a particular pulp mill or other industrial/municipal plant, where the toxicity emission rate (TER) is:

$$TER = TU \times \text{daily discharge volume } (m^3/d)$$

This approach is also useful for comparing the relative quantities of toxic material (sometimes referred to as toxic loading) discharged daily to the environment by various industries or mills with differing processes/treatment systems and water use etc. TER calculations provide a means to compare and assess relative differences in toxic loadings discharged daily to the environment by one or more mills. Such comparisons are not possible where discharge volumes are ignored and implications of the potential environmental impact of these discharges are restricted to a consideration of the effluent samples' LC50 values. Additionally, monitoring or regulatory guidelines based on TER values eliminate any attempt to meet discharge requirements merely by effluent dilution (McLeay 1987).

For the process engineer, the quantity of toxicity generated per unit of production frequently is important in evaluating mill operation and/or process design modifications. These data are derived by dividing toxicity emission rates by the daily tonnage (ADt) to yield a toxicity emission factor (TEF) (Wong et al. 1978, 1981; Holmbom & Lehtinen 1980; Voss et al. 1981; Nikunen 1983). However, these TEF values are not directly relevant to effluent quality *per se*.

$$TEF = TU \times \text{daily discharge volume per unit of production } (m^3/ADt)$$

The toxic unit concept has been used to assess the relative contribution of in-plant subprocess streams to overall toxicity of the final effluent discharge. This approach assumes that the toxic contributions of individual process streams are additive when the streams are combined. Toxicity-balance studies have demonstrated that this was not always the case (Bruynesteyn, 1977; Metikosh 1979).

Toxic units have also been used in attempts to develop a chemical approach for predicting the acute lethal toxicity (to fish) of pulp mill effluents (Leach et al. 1979; Holmbom & Lehtinen 1980; Leach & Chung, 1980). According to this approach, the concentration of each individual toxicant in the effluent is determined by chemical means. Then the toxic contribution (TU) of each of these toxicants is calculated as follows (Leach et al. 1979):

$$TU = \frac{\text{concentration of constituent in effluent}}{\text{96-h LC50 of constituent}}$$

The sum of the toxic unit contributions of the various individual toxicants is taken as the overall toxicity of the solution. Holmbom & Lehtinen (1980) determined that, for 7 of 12 mill subprocess samples examined, more than half of the toxicity of kraft bleach plant effluents was unaccounted for by chemical assay. Inasmuch as TU and TER values are derived from the results of LC50 bioassays, these values are *not* absolute measures of toxicity (McLeay 1987). Rather, they are relative values, and are subject to the effects of those same controlled or uncontrolled test variables that influence the LC50. The LC50 bioassay's inability to demonstrate acute or chronic sublethal toxic effects is also integral in toxic unit and toxicity emission rate values.

In summary, the LC50 value and the toxic unit are quantitative yet relative (test-dependent) measures of the concentration and amount of toxicity, respectively, which do not require that the identity or concentrations of the chemical constituents are known. Additional information is required before the biological impact of a particular discharge on receiving waters can be assessed. This includes an understanding of water chemistry, differing sensitivities of indigenous fish or other aquatic biota, and sublethal toxic effects caused by their acute or chronic exposure. Unless these variables are considered, LC50, TU, TER or TEF values derived by bioassay tests with rainbow trout or other aquatic species (Voss et al. 1981) are subject to misinterpretation if used to assess the likelihood of lethal toxic effects within the environment.

3.1.3 Acute and short-term bioassays with Daphnids

Daphnia are freshwater micro-crustaceans (zooplankton) that commonly occur in cool or warmwater lakes and streams. These organisms often comprise a major source of food for juvenile salmonid and other small resident freshwater fish species. Daphnids are easily cultured under laboratory conditions, and are now used routinely in Scandinavia, North America, and elsewhere for evaluating the aquatic toxicity of effluents and chemicals (OECD, 1984). *Ceriodaphnia dubia* is more and more used instead for *Daphnia magna* or *Daphnia pulex*. In Sweden also another zooplankton species, the brackish water harpacticoid species, *Nitocra spinipes*, is commonly used for testing effluents discharged into the Baltic Sea (Bengtsson 1978).

Standardized laboratory procedures and guidelines for measuring the acute toxicity for effluents or chemicals to *Daphnia* are available (for example OECD 1984, SFS 1994). All these procedures are similar, except for some pertinent differences such as the source and characteristics of the diluent water and culturing media. The *Daphnia* bioassay has two specific advantages. It evaluates the tolerance of a fish-food organism to an effluent or discharge. Also, it is simple and low cost, requires a minimum of effluent sample, and is suitable for on-site evaluations of in-plant toxicity or the efficacy of effluent treatment (Tunstall & Solinas 1977; Schmaltz 1979; Cary & Barrows 1981; Donnini, 1981,1983; Voss et al. 1981).

Basic test procedures are similar to those for the LC50 fish bioassay, except that bioassay solutions are not aerated and exposures normally are for 48 hours.

Since death is difficult to discern for such small organisms, especially in a coloured effluent, the bioassay determines the median effective concentration (EC50) of effluent which causes complete immobilization of 50% of the exposed organisms.

3.1.4 Luminescent bacteria bioassay (Microtox)

A number of bioassay tests using bacteria have been developed for rapid screening of the toxicity of aquatic contaminants (Dutka & Kwan 1981; Williamson & Johnson 1981; OECD 1984; Van Coillie et al. 1984). One of these luminescent bacteria bioassays, known also as "Microtox" (Beckman Instruments Inc.) has been examined with various chemicals and industrial effluents including pulp mill effluents (van Aggelen 1982; Blaise 1984; McCubbin 1984; Ahtiainen et al. 1994; Priha 1995, in press). This test determines the median effective concentration of effluent or chemical which inhibits light production by the luminescent marine bacterium Vibrio fisheri. The concentration-dependent extinction of light output is thought to reflect the effluent's effect on cellular respiration, although the exact mechanism(s) is not understood (Chang et al. 1981). The principal desirable attributes of the luminescent bacteria bioassay are its rapidity (< 1 h) and small (< 5 mL) effluent volume requirements.

Some instances of large intra- and inter-laboratory errors in reproducibility for Microtox assays with chemicals have been reported (Dutka & Kwan 1981). The quality of the bacterial cell suspensions was implicated. However, replicate tests with the same bacterial culture normally provide EC50 values which deviate no more than 10% (de Zwart & Sloof 1983). A number of investigators (se McLeay 1987, for references) have compared the Microtox assay with LC50 fish bioassays or EC50 tests with Daphnia or algae, using various diverse aquatic contaminants. In comparative bioassays with 15 chemicals, de Zwart and Sloof (1983) determined that, despite various inconsistencies, rainbow trout and Daphnia magna were, on average, 2.0 and 2.5 times respectively more sensitive than Microtox.

3.1.5 Acute and short-term algal bioassays

Diverse bioassays have been conducted to ascertain the effects of pulp and paper mill effluents on the production of freshwater algae i.e. aquatic organisms at the bottom of the food chain. Studies reported include bioassays with the green algae *Selenastrum capricornutum*, *Ankistrodesmus falcatus* and *Scenedesmus sp* (see McLeay 1987). Algal bioassays, usually *Selenastrum capricornutum*, are nowadays routinely included in short-term bioassays in countries like Sweden, Finland and North American countries.

3.1.6 Sublethal responses to acute and prolonged exposure

A number of different sublethal endpoints have been used to study the effects of exposure to pulp and paper mill effluents (Table 4). The overwhelming majority of the studies have been made on fish (McLeay 1987; Owens 1991), although some studies also include effects on other organisms such as mussels and crustaceans (Södergren 1991, 1993). A summary of extended laboratory experiments has been compiled in Table 4.

Table 4. Compilation of endpoints measured at extended laboratory exposures.

Species	Endpoints
Pike (Esox lucius)	egg mortality
Blenny (Zoarces viviparus)	egg number and larval growth
Sheepshead minnow (Cyprinodon variegatus)	embryo and fry mortality
Rainbow trout (Oncorhynchus mykiss)	larval survival, growth; energy metabolism; hematology; histopathology; MFO enzyme induction
Goldfish (Carassius auratus)	Sex hormone levels
Fourhorn sculpin (Myoxocephalus quadricornis)	Skeletal deformities; vertebral biochemical composition; hematology; energy metabolism
Bleak (Alburnus alburnus)	Skeletal deformities; vertebral biochemical composition
Chinook salmon (Oncorhynchus tshawytscha)	mortality; growth; hypoxia and histology

Bioassays determining effects on reproduction and fry survival of the zebra fish are commonly used in Finland and Sweden. Other studies have involved histological and morphological changes in salmonid fish. By means of histopathological studies structural changes and lesions in tissues are determined. In addition to histological damages studies of the effects on the physiological and biochemical level have been conducted (Lehtinen 1995, in press; Owens 1991).

3.2 Predictability of single-species tests

Presently environmental regulators, for their decisions, largely rely on data combined from a set of different single-species toxicity tests with different end-points (Cairns & Niederlehner 1987). Such species, used for toxicity testing in the laboratory, are frequently claimed to represent the most sensitive species. Thus, no observable effect concentrations for these species would be considered safe for the whole ecosystem. This kind of view has been challenged by scientists during the last decade (Cairns 1983; Cairns & Niederlehner 1987; Cairns et al. 1992; Crossland & LaPoint 1992).

Cairns (1983) has questioned whether single-species tests can be reliably used to predict responses at other levels of biological organization. Probably less than 1% of all freshwater species can be maintained in the laboratory sufficiently well to fulfill the requirement that no more than 10% of the control organisms expire during the tests. Thus, it seems unlikely that the most sensitive species are selected for testing. There are a number of other factors complicating extrapolation of laboratory results to the ecosystem. Especially in arctic/boreal regions the conditions in the laboratory do not resemble those in nature very much (both in terms of species and physical-chemical conditions). The laboratory test is based on strictly controlled physical-chemical conditions (static temperature, static oxygen level etc.). The strictly controlled experimental conditions are at the same time a prerequisite in order to gain comparable data from tests with other toxicants. Such tests certainly defend their position if the original objective was to rank the relative toxicity of different toxicants or waste waters, but the scientific justification of using single-species tests to predict changes in competition, predation, community function, ecosystem energy-flow and nutrient cycling, is questionable (Cairns 1983).

Cairns et al. (1992) also state that test species are often selected on the basis of their adaptability to laboratory conditions rather than on their occurrence in ecosystems. Species vary greatly in their sensitivity to a particular stress, and clearly no one species is "most sensitive" in all cases (Cairns & Niederlehner 1987; Cairns 1983). Testing with a series of species representing different taxonomic and functional groups allows for effect concentrations to be more precisely estimated. However, even the use of multiple, single species tests do not allow for effects on higher level processess (e.g. biomagnification, competition etc.) to be directly evaluated.

Conditions under which laboratory tests are conducted are different from the natural environments in several ways (beside geographical differences). Species are tested in the absence of competitors, predators or parasites that may reduce individual health and/or fitness. Individuals chosen for testing are those deemed to be free of diseases or other conditions (e.g. resource limitation), which might increase susceptibility to stress under natural conditions (Cairns et al. 1992).

Kock and Kuiper (1981) and Lundgren (1985) have summarized some instances where single-species laboratory tests fail to provide enough information to predict ecosystem effects:

There is a difference between the dose introduced under laboratory conditions and the dose reaching the biota under natural conditions, which among other things depends on:

- difficulties regarding the chemical form of pollutants, as modification of substances may take place;
- differences between the duration of many laboratory routine tests (often 48 or 96 h) and the much longer time scale for the action of persistant pollutants in nature. This is especially important for organisms with long life cycles;
- the unrealistically high concentration of pollutants applied to establish easily measurable (e.g. LC50 values), whereas in nature sublethal effects at much lower concentrations may have significant consequences.
- the testorganisms are not feeding on natural food items in the laboratory test, thus omitting one potentially important exposure route.

Single-species tests may be used for rapid screening of the toxicity of waste waters and chemicals. When combined with proper evaluation of chemical properties of substances and waste waters, they supply information on what may need further testing. As such they form the first tier in a multi-tiered assessment program consisting of a) short-term laboratory bioassays, b) medium-term laboratory studies at environmentally relevant concentrations focussing on sensitive lifestages of the test organisms (Neilson et al. 1990), c) model ecosystem studies under controlled environmentally realistic conditions and d) field studies consisting of both monitoring and specific evaluative studies in the receiving waters (Tana et al. 1994).

3.3 Multi-species testing, model ecosystems

Different types of both freshwater and marine model ecosystems have been used to evaluate effects of pollutants (see Lundgren 1985, for references). In the beginning of the 1980s, a systematic research of bleached kraft mill effluent impact in multi-species model ecosystems simulating the Baltic Sea littoral zone was initiated (Rosemarin et al. 1990a; Lehtinen et al. 1991). The reasons behind the application of the model ecosystem technique was an increased awareness of the fact that predicting environmental impact is not possible by only using single-species tests, which describe effects on individuals of one species. In order to obtain relevant, and for the environment more realistic data, a broader understanding of the structure *and* function of the ecosystem is needed. This includes an understanding of both direct effects of pollutants and indirect effects (responses) elicited by changes in species interactions under polluted conditions.

Model ecosystems may be defined as simplified copies of natural, or parts of natural ecosystems. An ecosystem consists of the physical environment formed by water, bottom substrate (sediment, stones), soluble particles in the water etc., and the biotic components consisting of microorganisms, plants and animals. From the solar energy, water, carbon dioxide, and minerals/nutrients, plant biomass is formed, which serves as food for the lowest consumer level, the primary consumers (grazers). The grazers and the predators (secondary consumers) form a relatively small part by quantity or by energy content but they are functionally of great significance due to their regulatory function of the primary producers. Finally, the microorganisms (bacteria, fungi, certain animals), consumers of dead organic material (detritus) serve as decomposers and liberate minerals and nutrients for production of new plant material.

Ecosystems vary in complexity, all from low complexity systems such as the Baltic Sea, to systems with very high complexity such as tropical coral reefs. Thus, the degree of ecosystem complexity will pose varying degrees of experimental hardship when it comes to simulating it in model ecosystems.

3.3.1 Promises and limitations of model ecosystems as compared with other methods

Generally, it is expected that ecotoxicological tests shall produce useful data on which realistic prognoses on the fate and effects of chemical substances in the environment can be made. Correctly used, the tests shall identify a potential environmental impact of a chemical or a complex effluent before the effect has been manifested in the environment (Landner et al. 1989). The limitations of short term, single-species test was discussed earlier. When it is question about different designs of model ecosystems, there are a number of critical questions that have to be considered:

- Is the system to be designed for studies on transport and distribution of chemicals, effects of chemicals, or both?
- Are the effect studies to be performed on the community- or the ecosystem-level, i.e. how many trophic levels will be contained in the system?
- Which environmental compartments or subsystems should be included: the pelagial (the free water mass) or the benthic subsystem, the littoral or deeper bottom areas?
- Is the system to be constructed under artificial laboratory conditions or should the system be constructed by transplanting intact set-ups of organisms from nature or enclosures of parts of nature?

- In case enclosures with intact set-ups are used, should they be completely isolated from the mother system during the experiment or should they stay in contact by continuous exchange of the medium?
- Should the testsystem be kept under constant environmental conditions regarding light, temperature, water current etc., or should it be exposed to natural climatic variations?
- What size of the system is needed (microcosm, mesocosm) and for how long time should exposure be maintained?
- Which property is most important: the realism of the system or its reproducibility and what optimal combinations are possible?
- Should the test parameters be chosen so that they can be applied both in the test system and in the field, i.e. for verifications studies?

There are no simple answers to the questions raised. If the aim of developing multi-species testsystems is to generate data necessary for **realistic predictions of the fate and effects of pollutants** in natural ecosystems, to be used in the framework of environmental hazard assessment, there might not be a great variety of ways to go (Landner et al. 1989).

The littoral, brackish-water model ecosystems to be described here in more detail (as well as systems used elsewhere) are established by transplanting an intact part of the littoral, containing both plant and animal elements, into land-based containers (Bokn et al. 1981; Notini et al. 1977, Kitchen 1979). For description of other types of model ecosystem set-ups the reader is referred to Landner et al. 1989, Lundgren 1985 and Tana 1991.

The littoral systems, which are equipped with a continuous water renewal, are relatively stable and experiments can be maintained over years (Landner et al. 1989). Thus, the systems contain a large degree of realism. However, economical and practical restrictions may prevent a wide use of large-scale model ecosystems in environmental risk assessments of pollutants. The degree of realism and prognostic value versus cost of single-species tests and model-ecosystem tests are illustrated in Figure 7.

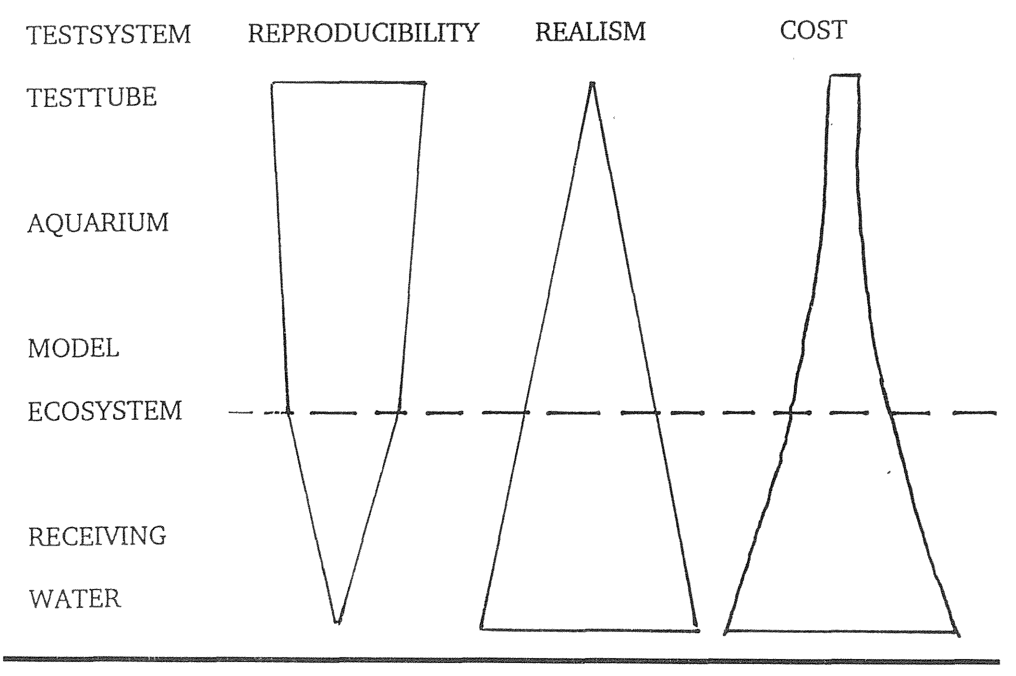


Figure 7. Reproducibility, realism and cost for different experimental approaches in hazard assessment protocols.

It may, for example, not be possible to test a chemical substance over a broad range of concentrations and replicates. A lower realism would increase the number of replicates, but a high degree of realism is, on the other hand, of vital importance if the results are intended for use as prognostic tools in the natural ecosystem. Realistic model ecosystems are well suited for studies on the fate of chemicals. Transformations and flows of chemicals can be followed and "key mechanisms" and "weak links" identified.

Besides effects on population level, effects on community and ecosystem levels can be analyzed, including secondary effects due to changes of energy flow and nutrient dynamics. Moreover, large (mesocosm) model ecosystems have a potential to validate prognostic computer models (Landner et al. 1989).

Cairns et al. (1992) reviewed results from model ecosystem tests (microcosms) and their correlation with results from single species tests (Table 5). Although the data in Table 5 do not show the details of the results from each of the studies, it does, however, provide a summary that indicates several important points.

Table 5. Summary of predictive toxicity tests using multispecies design, and correspondence between those findings and findings relying on single-species tests. (Source: Cairns et al. 1992)

Study	Toxicant	Estimated Toxicity (µg/L)	Comparison with Standard Lab Tests	Field Validation
Niederlehner et al.	Cadmium	MATC[a] = 0.20	Acute MATC = 42 Chronic MATC = 0.82	NA
McCormick et al.	TFM	MATC <100 (stimulatory)	LC25 for several fish species: 5,000–44,000	NA
Pratt et al.	Copper	LOEC[b] <6.6–36.5 MATC <6.6–26.7	LOEC for several species: 6.1–60.4, chronic MATC = 8.2	NA
Pratt et al.	Zinc	LOEC <4.2–89.2 MATC <4.2–51.6	Average LOEC for several species = 47, chronic MATC = 47	NA
Pratt et al.	Chlorine	LOEC <2.1–261 MATC <2.1–176	Average LOEC for several species = 3.4, chronic MATC = 11	Field microcosms MATC = 6–144
Pratt et al.	Atrazine	MATC = 17.9–193	MATC = 71–3,400	NA
Pontasch et al.	Effluent	LOEC = 1%	Acute daphnids and fish LC50: 18.8–63.1% Chronic daphnids:1% (using a 1% application factor)	Stream invertebrate responses predicted by lab tests
Pratt et al.	Phenol	LOEC = 300–23,300+	Several chronic single species LOEC = 2,600	NA
Niederlehner and Cairns	Ammonia	LOEC = 10–430 MATC <10–260	Several chronic single species LOEC = 2–612 MATC = 28	NA
Pratt and Bowers	Selenium	MATC = 14.4	Daphnid and fish MATCs = 180–360	Lotic field mesocosm MATC = 17.7

Note: Ranges of values for multispecies tests are based on responses of varying numbers of structural and functional parameters in the same test.

[a] MATC = maximum allowable toxic concentration.
[b] LOEC = lowest observable effect concentration.

First, a comparison of the results of the multispecies tests with those generated using standard laboratory protocols indicates that no consistent correspondence between reponses at different levels of biological organization can be assumed. Multispecies tests are not consistently more sensitive than single-species. However, effects on community- and ecosystem-level processes are frequently detected at chemical concentrations that have been deemed "safe" (i.e. associated with an acceptable risk) by the U.S. Environmental Protection Agency largely on the basis of effects data from single species tests (Cairns et al. 1992). These results illustrate the need for incorporation of tests at different levels of biological organization into the predictive tier of testing.

A second, equally important conclusion from Table 5 is that multispecies tests provide information on the nature of environmental impact that would rarely be indicated by standard single species test results. Generally, this contention is illustrated by experimental data documenting the variability in the relative sensitivity of ecosystem structure and function to different forms of stressors. For example, whereas structural changes were judged more sensitive to certain types of effluents, functional attributes may be much more sensitive to other toxicants.

An essential requirement for toxicity tests at any tier of the hazard evaluation process is that the results be reproducible among trials. Such evidence is accumulating both for responses determined using communities collected from the same ecosystem at different times (Niederlehner & Cairns 1990) and from different ecosystems at similar times (Pratt et al. 1989). More information in this area is needed.

3.3.2 Experimental set-up of littoral brackish water model ecosystem

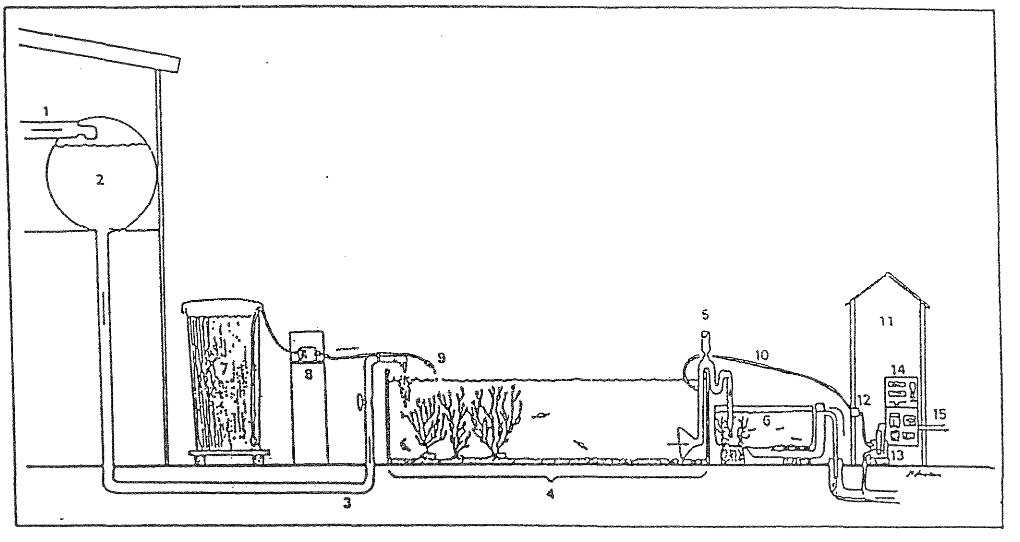
The littoral model ecosystem technique used for testing various pulp mill effluents in Sweden and Finland since the beginning of the 1980s consists of out-door land-based circular pools with an 8 m^3 water volume. Principally the systems are established by "transplanting" part of the mother system (both plants and animals) into the respective pools. This procedure poses demands on how and what is transplanted in order to avoid disturbance on the mother ecosystem and comparative studies between the model ecosystem and the mother ecosystem are anticipated (Landner et al. 1989).

The main biotic component of the littoral model ecosystem is the bladder-wrack, Fucus vesiculosus L., a brown alga important for the Baltic Sea littoral ecosystem. The bladder-wrack constitutes about 90% of the biomass of the Baltic littoral zone suitable for this alga. An advantage of studies on this community, apart from its function as the ecologically most important sub-system of the Baltic, is its relatively low diversity as compared with many other marine communities. Thus, the goal has been to build a community as complete as possible. The main emphasis has been on studies of the benthic (bottom) community, whereas less emphasis has been put on pelagic components (phyto- and zooplankton) (Lehtinen et al. 1992; Lindén et al. 1987).

In addition to the organisms directly associated with the bladder-wrack, a number of other free-swimming animal species are introduced into the model ecosystems. This especially concerns brood of the three-spined stickleback, Gasterosteus aculeatus. After the start-up, the model ecosystems are allowed to stabilize for 2–3 weeks before commencement of pollutant exposure. In additon to plants and animals introduced into the model ecosystems, smaller pools may be connected to the outgoing water from the model ecosystems for specific studies on, for example, fish physiology.

The mother ecosystem, simulated in the model ecosystem, is a typical small bladder-wrack dominated sheltered bay with a bottom substrate consisting of stone, sand and gravel. The stones serve as substrate for the sessile bladder-wrack. Under natural conditions greater water volumes will pass through the benthic mother ecosystem than in the model ecosystems. Adjustment of the plant biomass is therefore an important factor in order to maintain the similarity with the mother system where the water current supplies the plants with necessary nutrient even under low nutrient periods. The importance of the water flow for the growth of the bladder-wrack in the model ecosystems was studied in detail by Landner et al. (1989). The experimental set-up is schematically presented in Figure 8.

The effluent dilutions used in the model ecosystem tests of pulp mill effluents have been 400 and 2 000 times respectively, with one exception when the dilution was 200 and 1000 (Tana et al. 1994). The discharge volumes and daily production were considered, based on the TEF-concept described in section 3.1.2, in order to obtain comparable dilutions between different mills. The 400 times dilution has been chosen in order to describe the dilution conditions 1–2 km outside the immediate mixing zone along the coast of the Baltic. The 2 000 times dilution usually occurs 4–6 km from the discharge point.



1. Incoming water
2. Seawater tank
3. PEH-pipe to the pools
4. Mesocosm pool
5. Siphon for out-going water
6. Rainbow trout pool
7. Effluent container
8. Membrane pump
9. Dosage of effluent water
10. Tube to the measurement unit
11. Measurement unit
12. Magnetic valve
13. Registration electrodes
14. Measuring device
15. To the computer

Figure 8. Schematic descripition of the model ecosystem set-up.

Effluent characteristics and effects of individual compounds

4

4.1 Nature of the compounds produced during pulp production

The chemical bleaching of pulp produces a complex mixture of degradation products of residual lignin and other components such as wood extractives. The organic material in bleached kraft mill effluents exhibits a molecular weight distribution ranging from various types of monomeric compounds to large molecules with complicated chemical structures having molecular weights in the order of 10 000–30 000 g/mol (Pellinen & Salkinoja-Salonen 1985, Mörck et al 1991). The molecular weight distribution may vary somewhat depending on the wood species (Mörck et al. 1991) and bleaching process used (Yin et al. 1989). The effluents from the production of bleached hardwood kraft pulp contain organic material of lower average molecular weight than the corresponding softwood effluents (Mörck et al. 1991, Yin et al. 1989). Introduction of oxygen delignification in modern mills lowers the molecular weight of the organic material in the effluents as compared with effluents from mills with older kraft bleaching sequences (O'Connor et al. 1993, Yin et al. 1989, 1990).

A large part of the organic material in bleached kraft mill effluents is found in the high molecular weight fraction (Mw>1 000). Some characteristics of this material are listed in Table 6 (Dahlman & Mörck 1993).

Table 6. Characteristic properties of the high weight fraction of the organic material in kraft bleaching effluents (Source: Dahlman & Mörck 1993).

The high molecular weight fraction (Mw>1000):

- is mainly composed of strongly oxidized material, originating from lig-nin with high contents of olefinic structures and carboxylic acid groups. These oxidized and degraded lignin residues are mainly of an aliphatic nature, but contain minor amounts of phenolic structures,
- contains oligo- and/or polysaccharides, mainly originating from hemicelluloses,
- carries a large part of COD
- carries a large part of the organically bound chlorine,
- carries the major part of colour,
- is probably biologically inactive and non-toxic.

The high molecular weight material carries a large part of the COD and AOX found in bleach plant effluents, especially after biological treatment. Degradation studies carried out on high molecular weight organic materials originating from modern bleaching processes indicate a low degree of chlorination (Mörck et al. 1991). The chlorinated material is also difficult to distinguish from natural chlorinated material. These results therefore suggest that it is unlikely that degradation in the receiving water of high molecular weight organic material discharged from kraft mills equipped with modern bleaching technology should lead to formation of highly chlorinated monomeric phenolic compounds (Axegård et al. 1993, Dahlman and Mörck 1993). Some recent studies suggest, however, that the portion of high molecular weight material is less than previously thought because the low molecular weight material (Mw<1 000) associates and forms molecular aggregates which appear as high molecular weight material (Jokela & Salkinoja-Salonen 1992).

Degradation studies have shown that the same types of chlorinated phenolic structures found in high molecular weight material in pulp mill effluents are found also in naturally occuring humic materials isolated from industrially unpolluted surface waters and ground waters (Dahlman et al. 1993b,c). It may therefore be expected that degradation of high molecular weight effluent constituents and naturally occuring humic materials in aquatic environments should give rise to similar monomeric phenolic dagradation products (Axegård et al. 1993).

The more important types of low molecular weight organic material so far identified in bleached kraft mill effluents are presented in Figure 9 (Dahlman & Mörck 1993).

The identified compounds can be roughly separated into three main classes: Acids, phenolic compounds and neutral compounds. The phenolic compounds and some of the acids are degradation products and oxidized fragments originating from residual lignin in the pulp, whereas other types of compounds such as resin acids, fatty acids, terpenes and sterols are residues of extractives carried over to the bleaching plant with the pulp (Dahlman & Mörck 1993).

In effluents from old kraft mills with conventional bleaching technology, many types of compounds could be present in both their chlorinated and non-chlorinated forms, whereas effluents from kraft mills equipped with modern bleaching technology contain fewer chlorinated compounds and with a generally lower degree of chlorination (Dahlman & Mörck 1993).

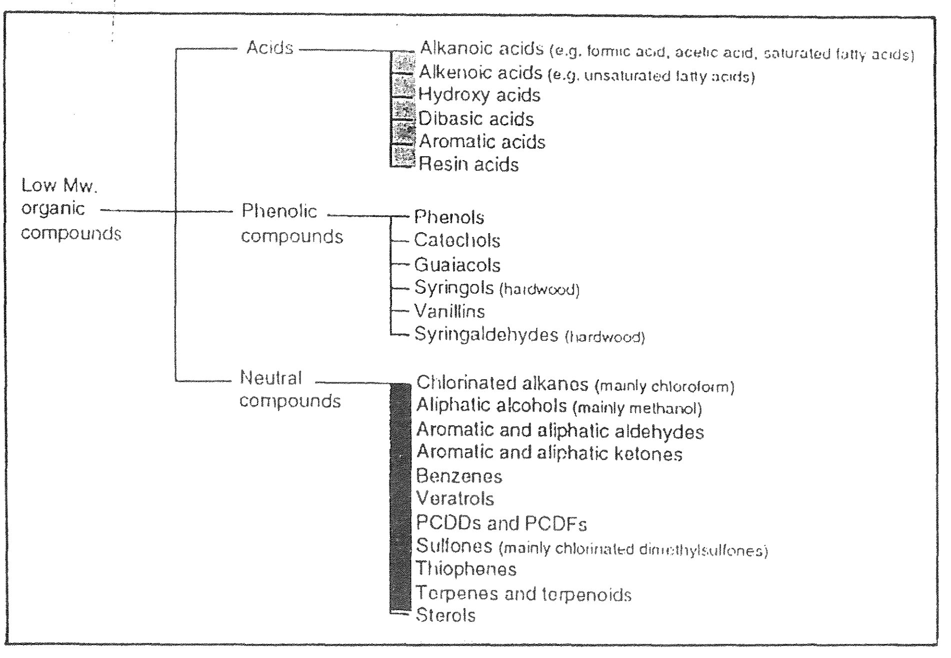


Figure 9. Important classes of low molecular weight compounds identified in bleached kraft mill effluents (Source: Dahlman & Mörck 1993)

In order to compare process technologies and process modifications, results from a comprehensive chemical characterization of three bleached kraft mill effluents are presented in Figure 10 (Dahlman & Mörck 1993). The three different effluents originated all from production of fully bleached softwood karft pulp representing three levels of process technology. Level A corresponds to the introduction of pre-bleaching technology i.e. oxygen delignification, whereas level B corresponds to combination of pre-bleaching and low chlorine multiple, a 30 % substitution of chlorine dioxcide and reinforcment of the alkaline extraction stages with oxygen and hydrogen peroxide. The effluent representing level C had the same technology found at level B but the effluent was secondary treated in an aerated lagoon.

Figure 10 shows that the biologically treated (aerated lagoon) effluent studied (level C) contains much smaller amounts of low molecular weight organic compounds compared to the effluent without secondary treatment (level B). Same kind of results, or even better can be achieved by using activated sludge plants as secondary treatment.

4.1.1 Hydrophobic substances

The main emphasis in chemical characterization studies of pulp mill effluents has been in studies with organochlorine susbtances. Hydrofobic compounds are of major concern because of their potential to bioconcentrate in organisms. If they are also persistent, they may move through the food chain to other organisms.

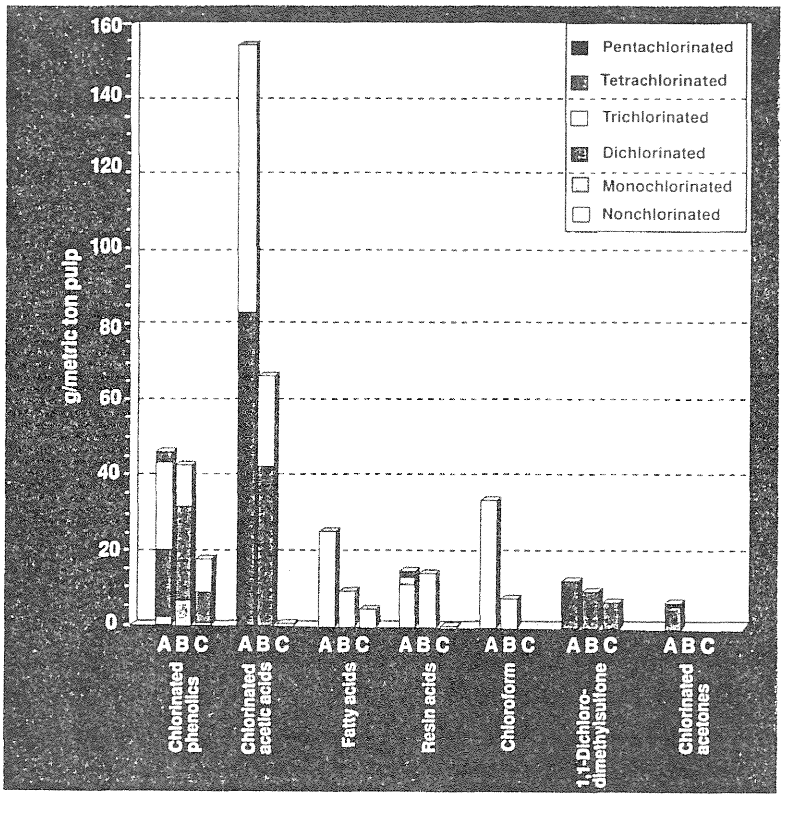


Figure 10. Quantities of chlorinated phenolic compounds (phenols,guaiacols,cathecols) chlorinated acetic acids, fatty acids, resin acids, chloroform 1,1-dimethylsulfone and chlorinated acetones in kraft mill effluents (Source: Dahlman & Mörck 1993).

Highly chlorinated compounds, such as PCDDs (polychlorinated dibenzo-p-dioxins) and PCDFs (polychlorinated dibenzofurans), and polychlorinated phenols, have a greater potential of bioaccumulation and are more persistent than their lesser chlorinated counterparts.

After introduction of modern bleaching technologies with 70–100 % chlorine dioxide substitution and low chlorine multiple, there are few indications that more than trace quantities of hydrophobic persistent, chlorinated bioaccumulating compounds are produced during bleaching. In some cases, compounds of this type are below the measurable limit in final effluents but may be detected in individual bleach plant process streams (Solomon et al. 1993). For example, levels of 2,3,7,8-TCDD/TCDF, the most potent congeners are below the measurable limit (15 pg/l, ppq, in the case of 2,3,7,8-TCDD) in the final effluent as discharged (Luthe et al. 1992).

Paasivirta (1992) also observed that toxic dioxins and furans were formed in trace amounts in chlorination stage of pulp bleaching, but that their emissions, however, have been cut down by replacement of the chlorine with chlorine dioxide and by effective secondary treatment. Particlebound 3,4,6,7- and 2,3,7,8-tetrachlorodibenzothiophene were recently found at the detection limit of about 1 pg/l in the process stream from hardwood bleaching with 90% chlorine dioxide substitution (Sinkkonen et al. 1992). This level may be below the detection limit in final mill effluent. Since some of the PCDD/PCDFs formed in bleaching originate from naturally occuring non-chlorinated precursors, it is possible that measurable levels of mono-, di-, and trichlorinated PCDD/PCDFs are present, especially when low chlorine multiple is used to avoid the formation of the 2,3,7,8-isomer (Birkholz et al. 1993).

4.1.2 Chlorophenols

Chlorophenols have been studied in the greatest detail probably because they were originally identified as contributing to the acute toxicity of chlorine bleaching effluents and all the isomers can be analyzed by gas chromatographic comparison with standards. Formula of the most commonly found PCPs, PCGs and PCCs are shown in figure 11 (Paasivirta 1992). Chlorophenolic compounds are acutely toxic but not very highly bioaccumulative. They can be methylated by micro-organisms to more persistant and lipophilic chloroanisoles (PCA) and chloroveratroles (PCV) (Neilson et al. 1989, Herve 1990, Paasivirta 1992). Chlorosyringols and chlorosyringaldehydes occur only in hardwoods so they can only be found in effluents from hardwood bleaching.

The quantities and proportions of different types of chlorophenols change with increasing chlorine dioxide substitution because of the different manner in which chlorine dioxide and chlorine react with residual lignins. The total amount of chlorophenols found in bleach plant effluent from softwood pulp decreased from the range of 30–120g/t pulp at 70% substitution to about 1–10 g/t pulp or even far below that at 100% substitution assuming a chlorine multiple of 0.2 (Nikki & Korhonen 1983, Axegård 1986, Liebergott et al. 1991, Flink et al. 1993). At 70% chlorine dioxide substitution chlorinated catechols and guaiacols may constitute about 35% of the total phenols, whereas at 100% substitution chlorovanillin comprises about 90% of total chlorophenols formed in softwood bleaching (Liebergott et al 1991). The corresponding chlorosyringaldehyde is found in hardwood effluent (Smith et al. 1993). The remaining chlorophenols are mono-or dichlorinated. Tri- or more highly chlorinated phenols being either non-detectable or close to the detection limit (Dahlman et al. 1993a, O'Connor et al. 1993).

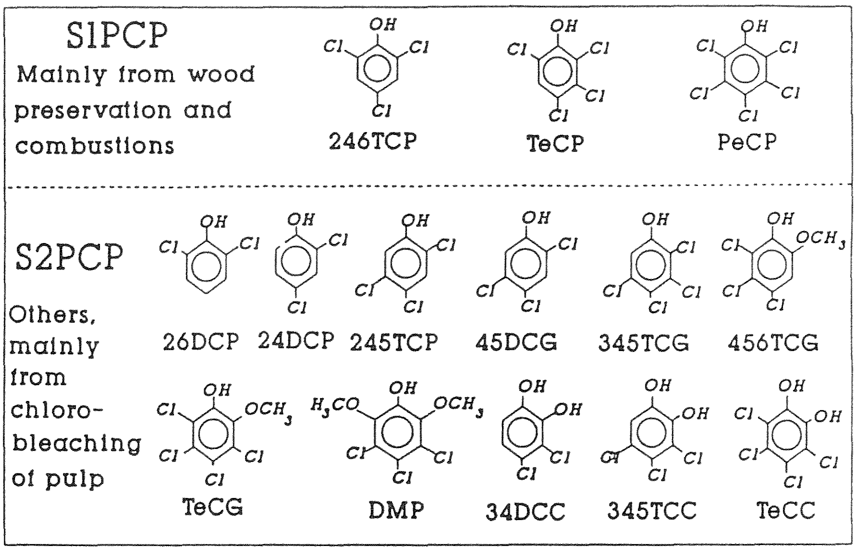


Figure 11. Most commonly found chlorophenols (Source: Paasivirta 1992).

Chlorinated organics, measured as AOX concentrations in receiving waters, decreased only slightly more than the dilution in the studied lake area (Holmbom et al. 1992). Thus the authors conclude that there is no extensive physical-chemical, biochemical or photochemical degradation of chlorinated organic matter nor any extensive sedimentation, in the area. Lake mesocosm studies, on the other hand, showed that the destruction of organic carbon and organic halogen (AOX) proved to depend on light (Salkinoja-Salonen et al. 1993, Saski et al. 1991). During summer and winter 30–80% of organic halogen (AOX) was removed from the waste water phases while only 1% was found in sedimented matter. Less AOX was removed from dark mesocosms than from light ones, but this difference was less prominent in humic waters. Thus the removal of organic halogen in lake ecosystems was concluded to be photochemical and biological degradation (Salkinoja-Salonen et al. 1993).

Chlorophenolics are found in mill effluents, recipient waters and sediments both in free and in bound (alkali hydrolysable) form. Both free and bound chlorophenolics are to most part freely dissolved in waters, not adsorbed to particles and the proportion of free phenolics decrease when going from the effluent to recipient waters and to sediments. Free chlorophenolics were found to decrease clearly more than the dilution in the recipient waters in a lake area where a study of environmental fate of effluent components was made (Holmbom et al.1992).

4.1.3 Resin acids and fatty acids

Resin acids are naturally occuring compounds in wood resins, particularly in pine and spruce. The amounts are particularly high in concentrated effluents from mechanical pulp production (Johnsen et al. 1993). If equally high amounts of resin acids are found in kraft mill effluent, their origin is frequently spills of black liquor and soap or black liquor carry-over. Resin acids are also found in lower concentrations in mills using recycled unbleached stock (Folke et al 1993a). In a study on a market bleached kraft mill, about 14 g/t pulp of resin acids, 8 g/t pulp of saturated fatty acids and 1 g/t pulp of unsaturated fatty acids were reported in untreated effluents (McCubbin et al. 1992).

Resin acids and unsaturated fatty acids were reduced below 1 g/t pulp by secondary treatment in an aerated lagoon. The discharges of resin acids found during the 1990 Canadian MISA monitoring program were quite variable. The mills with biological treatment systems which discharge low quantities of BOD, have very low resin acid discharge rates. Other mills have higher discharge rates with kraft mills also manufacturing mechanical pulp having the highest discharge (McCubbin et al. 1992).

The lipophilic extractives such as resin acids and fatty acids stay absorbed to particles in the effluents and maybe even more in recipient waters (Holmbom et al.1992). Thus the main process for their clearance from recipient waters is probably sedimentation. This binding to suspended material of lipophilic extractives may retard their microbial degradation and bio-availability.

4.1.4 Chelating agents

Chelating agents, e.g. EDTA are used extensively within the new pulp bleaching sequences using hydrogen peroxide or ozone but also in mechanical pulp production. Because these substances are discharged with spent bleach liquors from these bleach plants, some comments on these substances should be made.

Chelating or sequestering agents are usually large organic molecules that will bind metals in an inactive or temporary non-reactive form. Common chelating agents are EDTA and DTPA. In the literature, unrelated to pulp mills, the role of natural and artificial chelating agents in the functioning of ecosystems is described (Folke et al. 1993a). The natural ones have major functions in keeping trace nutrients dissolved in the water as a reservoir for algal nutrition.

In the course of the preparation of a detailed study of mechanical pulp and paper mills in Ontario the literature was searched without finding any evidence of harmful environmental effects of chelators used in pulp mills (Sprague et al. 1991). In a CTMP mill effluent about 38 mg/l of DTPA and 12 mg/l of EDTA was found, but concentrations in the river were never found to be above the detection level of 0.5 mg/l and no harmful effect was credited to the sequestrants (Sprague et al. 1991). A study on environmental effects of ECF- and TCF-bleached pulp mill effluents showed that in marine recipients

chelating agents were found only in the solid fraction of sediments and that concentrations were highest in sediments with high organic matter content (Puustinen and Uotila 1994). The amounts in recipient water were found to be below 0.005 mg/l and in sediments the amounts of chelating agents ranged between 0.5–600 mg/kg d.w. According to a litterature review (Langi 1994) chelating agents as a source of nitrogen in water systems will amount to less than 10%, a few per cent on an average of the natural nitrogen content of water systems. This could mainly become an issue in nitrogen limited waters. The use of complexing agents is not expected to cause heavy metals to be dissolved from sediments in the water system, but they probably will prevent the sedimentation of metals close to the discharge point, and metals will thus spread out over a larger area in lower concentrations.

4.2 Naturally occurring chlorinated compounds

Chlorinated organic compounds are not totally attributable to human activities but these compounds are formed by biological processes in nature (Neidelman & Geigert 1986, Gribble 1992). Compounds being chlorinated are for instance phenols, ketones, terpenes, sesquiterpenes and unsaturated compounds. Many of these natural organochlorines participate in defence mechanisms and as antimicrobial agents. In addition to biologically formed chlorinated compounds, naturally occurring chlorocompounds may be derived from forest fires and volcanoes. Dominating subtances from these processes are methyl chloride, chloroform and carbon tetrachloride (Enell & Wennberg 1990). A careful study of the ash from the 1980 eruption of Mt. St. Helens revealed three isomers of pentachlorobiphenyls (PCBs) representing the first discovery of a natural source of PCBs (Gribble 1992).

Recently, as a result of concerns that AOX was having adverse ecological effects, there have been efforts to determine if AOX occurs naturally. Asplund & Grimvall (1991), Grön (1990), Asplund et al. (1989), and recently Dahlman et al. (1993c), have investigated the levels and formation of "natural" AOX in soils, surface water, groundwater and sediments. Levels of AOX from 1 to 80 μg/l were found in aquifers unaffected by human activities. The sometimes very high background concentrations of AOX in water bodies is illustrated by a frequency distribution diagram based on 134 Swedish lakes that have no known point source (Figure 12). Concentrations of AOX ranging from 11 to 185 μgCl/l were found.

The highest concentrations were found in humic-rich, oligotrophic lakes in remote areas where the AOX concentrations were shown to be comparable to those in industrially polluted waters such as the Rhine River; along a profile from the source of this river to the Dutch border, AOX concentrations varied from 5 to 200 μg Cl/l. In a study from Lake Vättern it was observed that the mean AOX-concentration (32 μg/l) in unpolluted effluent river waters was higher than in the lake (15 μg/l) despite the fact that the lake is receiving bleached pulp mill effluent (Grimvall et al. 1991).

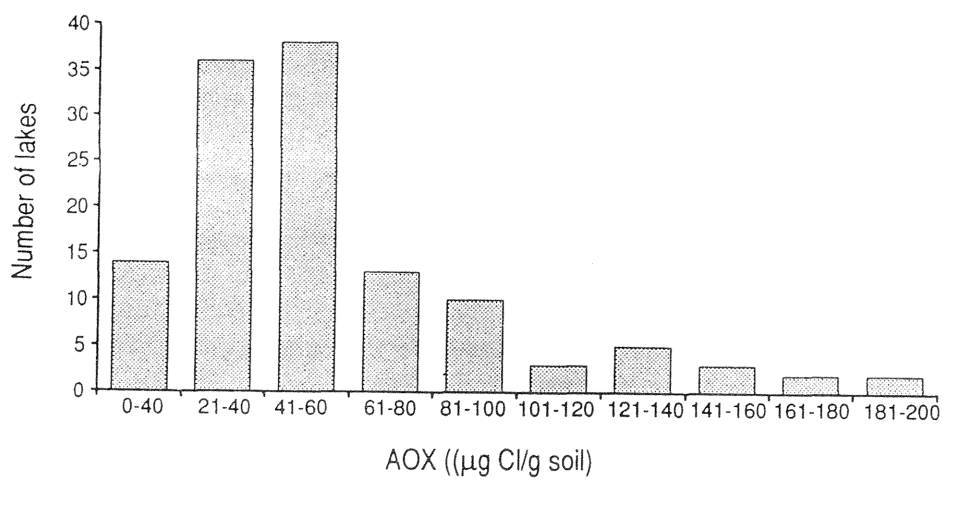


Figure 12. Concentration of adsorbable organohalogens (AOX) in 135 Swedish lakes (Source: Asplund 1992).

It appears that natural halogenation processes in water and soil introduce chlorine to fulvic and humic acids at a ratio of typically one (1) Cl for every 1 000 carbons. The natural AOX can be degraded chemically to form chlorinated, ethoxylated and methoxylated benzoic acid esters and thus, some of the chlorine is bound to aromatic rings in natural compounds (Dahlman et al. 1993b).

Attempts are being made to gain a perspective on natural vs industrial levels of AOX by compiling mass balances (Enell & Wennberg 1991, Grimvall et al. 1991) including atmospheric deposition. Although the mass balances of AOX are still in their infancy the available results for the Baltic Sea and the watershed of lake Vättern in Sweden demonstrate that the quantities of natural AOX are significant compared with industrial levels, that AOX must be fairly degradable with a half life of the order of a year and that there is long distance atmospheric and hydraulic transport of AOX.

4.3 Effects of individual compounds

Bioassays with the aim of assessing the toxicity of single substances in pulp mill effluents or groups of BKME-specific substances are still relatively scarce.

4.3.1 Chlorate

Bleaching with chlorine dioxide leads to formation of chlorate in amounts typically ranging from 1–6 kg/t pulp (Lehtinen et al. 1991). Increasing chlorine dioxide substitution tends to lead to higher chlorate discharges, as 10–15% of the ClO_2 used for bleaching dissociates into chlorate. Chlorate is easily removed in aerobic treatment plants that have anoxic zones, so it is not the amounts of chlorine dioxide used for bleaching that alone determines the amounts discharged. Apart from Scandinavia, little, if anything has been published regarding chlorate discharges (Folke et al. 1993a).

Chlorate has been shown to be lethal to brown algae such as the bladder-wrack which is a dominant, structuring compound in the sub-littoral ecosystem in the Baltic Sea (Lehtinen et al.1988). The chlorate-induced damage to this and other brown algae has been shown to cause secondary effects on the sub-littoral, hard bottom ecosystem as shown also in model ecosystem experiments (Lehtinen et al. 1988). The dissappearance of the bladder-wrack reduced the production of benthic macrofauna i.e. several species of invertebrates which grew in the bladder-wrack zone lost their ecological niche. Theorethically, it can be expected that the local dissappearance of the bladder-wrack might also result in a decreased recruitment of larvae of the free-swimming fish population. Conclusive data on this matter are lacking so far, however. The LOEC-levels (Lowest Observed Effective Concentration) for growth of bladder-wrack have been found to be 15–20 µg ClO_2/l (Rosemarin et al. 1994). The mechanism of chlorate toxicity to plants is related to its three-D molecular similar to nitrate (ClO_2 vs. NO_3). Thus, receiving waters that are nitrogen limited will be more vulnerable than receiving waters that are phosphorus limited with respect to primary biomass production. For other algae than brown algae chlorate has not been observed to cause deleterious effects (Rosemarin et al. 1994).

4.3.2 Chlorophenolics

In a review from 1987 (McLeay 1987) chlorophenolic compounds, namely chloroguaiacols, chlorocathecols and chlorophenols, arising from the bleaching of pulp, were shown to be normally present at sublethal levels in untreated whole mill effluents from bleached kraft and sulphite mills. Maximum total concentrations were normally in the range of 1 000–2 000 µg/l irrespective of bleaching variables. Biotreated effluents were found to contain chlorophenolics from detection limit up to 1 000 µg/l chlorophenols. In effluents from modern mills the concentrations of chlorinated phenols have been from detection limit to 400 µg/l, and in receiving waters the concentrations are at a level of 1 to 10 µg/l or below 1 µg/l (Holmbom et al. 1992, Tana & Lehtinen 1995, Paasivirta 1992, Flink et al. 1993). This shows that the concentrations in mill effluents since the middle of the 1980s have drastically diminished. Results from older studies do not, however, include mill and process data so the comparisons between different processes are difficult.

Chlorophenolics accumulate in organisms in the receiving waters (Landner et al. 1977, Oikari & Holmbom 1986, McLeay 1987, Paasivirta 1992). McLeay (1987) has presented comprehensive data regarding bioaccumulation of chlorophenols and resin acids in various tissues of organisms (Table 7). It is evident that the unchlorinated resin acids bioconcentrate at least as much as chlorophenols. Chlorophenols are readily taken up from the water by fish but are also rapidly excreted through the bile conjugated with glucuronic acid (Oikari & Holmbom 1986). More than 95% of the chlorinated phenols occur as conjugates in the bile of fish. Resin acids also are conjugated in the same way. It may thus be concluded that the risk for high level bioaccumulation of these substances must be considered as very small. This observation is supported by experimental work and field investigations (Lehtinen 1990, Lehtinen et al. 1990, Tana, et al. 1988, Landner et al. 1994b).

Chlorophenols, chloroguaiacols and chlorocathecols are transformed into chloroanisoles and chloroveratroles. Even though these transformation reactions quantitatively are of little importance, they are not insignificant (Neilson et al. 1991). Fish from the Baltic Sea have been found to contain tri- and tetrachloroveratrol up to 600 µg/kg fatty tissue.

Chloroveratroles and chloroanisoles have been observed to be very off-flavouric causing bad taste in pulp mill recipients to fish and incubated mussels (Paasivirta et al. 1992). The trend towards discharge of primarly lower chlorinated phenolics caused by the use of high chlorine dioxide substitution and low molecular chlorine multiples will reduce or eliminate this problem in the future.

Data from tests with single chlorinated phenolic substances in pulp mill effluents or chlorinated phenolics as isolated groups are relatively few. Renberg et al. (1981) studied the uptake and reproductive effects of chlorinated guaiacols and cathecols in fish and a crustacean. The results demonstrated a rapid uptake of the substances in fish and an equally rapid excretion so that analytical detection limit for the substance in fish tissue was reached after 10 days after discontinuation of the exposure. The addition of chlorinated phenols as pollutants to simulated KME did not increase or alter the observed effects on the energy metabolism of the fish after 3 months exposure (Oikari et al 1984a, 1985a). This indicates that chlorinated phenols in the mixture did not cause an increased toxicity besides the one caused by non-chlorinated substances contained in the soap mixture.

Table 7. Bioconcentration factors for different compounds present in pulp mill effluents (Source: McLeay 1987).

Chemical	Test concentration (µg/L)	Diluent water	Exposure (days)	Organism	Tissue	Tissue concentration[a] (µg/g)	BCF[b]
dehydroabietic acid	650	FW[c]	5	sockeye salmon	whole-body	19	30
					bile	647	996
					brain	620	954
					kidney	278	428
					liver	263	404
					carcass	8	12
dehydroabietic acid	400	BW[d]	5	amphipods	whole-body	8	20
dehydroabietic acid	1 200	FW	4	rainbow trout	plasma	237	198
					liver	101	84
					kidney	83	69
					brain	37	31
					muscle	16	13
resin acid mixture	1 400	FW	2	rainbow trout	liver	273	195
					kidney	88	63
					brain	82	59
					muscle	24	17
2,4-dichlorophenol	1 700	FW	1	brown trout	whole-body	18	10
trichlorophenol	800	FW	1	brown trout	whole-body	6	12
tetrachlorophenol[g]	500	FW	1	brown trout	whole-body	210	450
pentachlorophenol[g]	200	FW	1	brown trout	whole-body	200	100
4,5-dichlorocatechol	2 300	FW	1	brown trout	whole-body	10	4
tetrachlorocatechol	1 100	FW	1	brown trout	whole-body	6	6
3,4,5-trichloroveratrole[e]	10	FW	28	zebra fish	whole-body	350[f]	3 200
tetrachloroveratrole[e]	20	FW	56	zebra fish	whole-body	2 300[f]	25 000

a Determined on a wet weight basis except where indicated

b Bioconcentration factor. Most values presented are "apparent" rather than "true" BCF's since studies did not determine that state of equilibrium had been attained and water concentrations were monitored infrequently or not at all.

c Freshwater

d Brackish water (salinity 10–15 o/oo)

e Not found in effluent; but formed by bacterial methylation of tri-and tetraguaiacol

f values expressed as µg/g fat

g Present if used as slimcide paper mill effluents

Of specific compounds studied, which are directly or indirectly related to pulp bleaching some chlorinated phenolic compounds may be mentioned. Intraperitoneal injections of 4,5-dichloroveratrol, 4,5,6-trichloroguaiacol, 3,4,5-trichloroveratrol, tetrachloroveratrol and tetrachloroguaiacol did not induce transformation enzyme (EROD) activities exept for high doses (>100 mg) of tetrachloroveratrol, which caused a weak induction (Förlin et al. 1989). No effects were observed on conjugation enzyme activities except for high doses of 4,5-dichloroveratrole which inhibited the UDP-GT and glutathione transferase (GST).

Bengtsson et al. (1989) used tetrachloro-1,2-benzoquinone, an oxidation product of the corresponding catechol, as toxicant in a 4,5 month exposure with fourhorn sculpin, *Myoxocephalus quadricornis*. The concentrations used were 100 and 500 µg/l, respectively. Differences in vertebral mechanical characteristics were obtained as well as deformed and dislocated vertebrate (in high dose only). The doses used were high compared to those to be expected even immediately outside a pulp mill discharge. A chronic exposure of fish to 3,4,5,6- tetrachlorocathecol for 25 days resulted in most physiological parameters remaining at control levels with the exeption of leucocrit, which was elevated, cortisol, which was depressed, and disease resistance which remained impaired (Kennedy et al. 1994).

The fate and effects of the pulp mill effluent compound 4,5,6-trichloroguaiacol (TCG) were tested over 16 months on a model Baltic Sea littoral zone using a bladder-wrack, *Fucus vesiculosus*, based mesoscale model ecosystem (Rosemarin et al. 1990b). Bioaccumulation of TCG and metabolites from water ranged from 50 times for algae up to 700 times for invertebrates and fish, the factor increasing with trophic level. Algae contained chloroguaiacols, chlorocathecols and chloroveratroles and exhibited no major toxic effect. Bladder-wrack colonization appeared to be hindered by filamentous algae which covered surfaces otherwise available for new colonization. This unrestricted filamentous algal growth was probably a result of reduced grazing by herbivores, which in turn was apparently caused by reproduction failure in herbivorous crustaceans.

Sediment-dwelling organisms appeared less affected than invertebrates in the algal habitat, possibly bacause of reduced bioavailability of toxic compounds due to binding to sediment particles. TCG and metabolites in the sediment were dominated by catechols; no veratroles were found. Only in the largest size class of sticklebacks there was a dose-related reduction in mean weight. Only 0.5 % of the TCG was recovered in the system after 16 months. Of this 99% was associated with the sediment. The remainder was divided equally between algae and fauna. The role of algae and sediment in the Baltic Sea littoral zone is therefore paramount to the ultimate fate and effects of such compounds on invertebrates and fish (Rosemarin et al. 1990b).

4.3.3 Thiophenes

Another group of substances identified in kraft pulp mill effluents, chlorinated thiophenes were studied with respect to their bioaccumulation and toxicity towards fish and *Nitocra spinipes* (Lunde et al. 1992). According to the octanol-water partitioning coefficient these substances appeared to be rather bioaccumulative. The bioaccumulation coefficients were, however, found to be low and similar for all isomers of the chlorinated thiophene compounds and also lower than expected from the partitioning coefficients. They were also shown to have mutagenic capacity according to Ames' test. These substances occur in concentrations from 1.8 to 11.2 µg/l in effluents (Lunde et al. 1992), a level which must be considered as low and not of immediate concern even close to effluent outfall. It is evident that as in the case with polychlorinated phenolic compounds, bleaching with low chlorine multiple will decrease formation of polychlorinated isomers of thiophenes.

4.3.4 Resin acids and fatty acids

In the review by McLeay (1987) levels of resin acids in untreated pulp mill effluents often exceeded lethal limits. Reported total total concentrations in whole mill effluents ranged from 100–25 000µg/l in untreated kraft effluents and in untreated mechanical pulping effluents from 1 300–80 000µg/l. Biotreatment normally reduced resin acid concentrations to sublethal levels in effluents from all mill processes. Concentrations of unchlorinated resin acids usually decreased by 90% or more due to treatment, whereas chlorinated resin acids were more resistant to biological biodegradation (McLeay 1987). Fatty acids were reported in untreated whole mill effluents in total concentrations ranging from 20 µg/l (sublethal) to 22 000 µg/l (above acutely lethal levels). Biotreated effluents contained only sublethal levels of fatty acids, indicative of their facile biodegradation (McLeay 1987). Recin acid concentrations in effluents from modern mills are between detection limit and 1 000 μg/l. The concentrations found in receiving waters outside modern mills have varied between 0–5 μg/l (Holmbom et al. 1992, Robinson et al. 1994, Tana & Lehtinen 1995).

Oikari & Nakari (1982) found that simulated unbleached kraft mill effluents, containing a mixture of resin acids and fatty acids, caused liver dysfunction in trout, which was reflected by inhibited conjugation enzyme function, increased plasma bilirubin levels and major effects on respiration and energy metabolism in fish. Continued work by this group showed that toxic effects of dehydroabietic acid (DHAA) could be detected down to a concentration of about 20 μg/l DHAA (Oikari et al. 1983). Resin acids were also found to cause hematological effects in addition to inhibited activity of the UDP-GT conjugation enzyme in fish exposed for 30 days (Oikari et al. 1984b). Resin acids have also been observed to cause significant effects on both ion transport and hepatic uptake of bile acids (Råberg et al. 1992).

Tana (1988) found that a number of physiological parameters started to fluctuate around the control values when fish were exposed to pure chlorophenols, dehydroabietic acid or mixtures of these (Figure 13). Many of the responses, such as red blood cell indices, seemed to be of adaptive character. Some metabolic parameters, such as liver glycogen and plasma glucose rose at first, but decreased later, in particular the liver glycogen, indicating a disrupted carbohydrate metabolism in fish. The UDP-conjugation enzyme was continuously inhibited at exposure to 5 and 50 μg/l dehydroabietic acid, whereas the activity started to oscillate when mixtures of chlorophenolics and dehydroabietic acid (5 μg/l, respectively) were used. Obviously, resin acids may have more serious cytotoxic effects, being inhibitors rather than stimulators. These results were also in accordance with the inhibiting effects on UDP with resin acid mixtures, obtained by Oikari & Nakari (1982). The 5 μg/l level of dehydroabietic acid may be considered as the lowest effective concentration in the undiluted effluent from a modern mill. Resin acid concentrations analyzed from recipient waters below modern mills have been observed to range between 1 and 5 μg/l depending on the recipient. However, other resin acids do not necessarily show the same toxicity as dehydroabietic acid.

Niimi et al. (1992) reported bioconcentration factors of resin acids from 25–130 among fish exposed to waterborn concentration from 0,7–3,6 μg/l. The bioconcentration factor was reduced as the percentage of conjugation of the resin acids in the bile increased, pointing to this elimination pathway as the most important. Sublethal exposure of rainbow trout to 14-monochlorodehydroabietic acid (MCDHAA) and 12,14-dichloro-dehydroabietic acid (DCDHAA) for 24 hours resulted in a classical stress response including significant primary (secretion of corticosteroids), secondary (hyperlacticemia, hyperglycemia) and tertiary (reduced swimming performance and lowered disease resistance) effcets (Kennedy et al. 1994). Unfortunately the exposure concentrations were not presented.

It may be concluded that resin acids appear to be more responsible than chlorophenolics for the biological effects recorded at exposure to pulp mill effluents. The process modifications and introduction of biotreatment systems have greatly reduced the load of toxic materials including chlorinated phenols and resin acids during the recent years. A good example is the study from Lake Saimaa where the concentrations of chlorinated phenols decreased from 8–16 μg/l in lake water, depending on distance to below 1 μg/l after a new activated sludge treatment plant was taken into use (Kaplin and Holmbom 1994). Another example is from eastern Finland from river Pielinen where a an old fashioned kraft mill was replaced with a new mill using modern bleaching technology and producing both ECF and TCF bleached pulp. The mill is equipped with an effective secondary treatment plant. In spite of the triple increase in production the concentra-

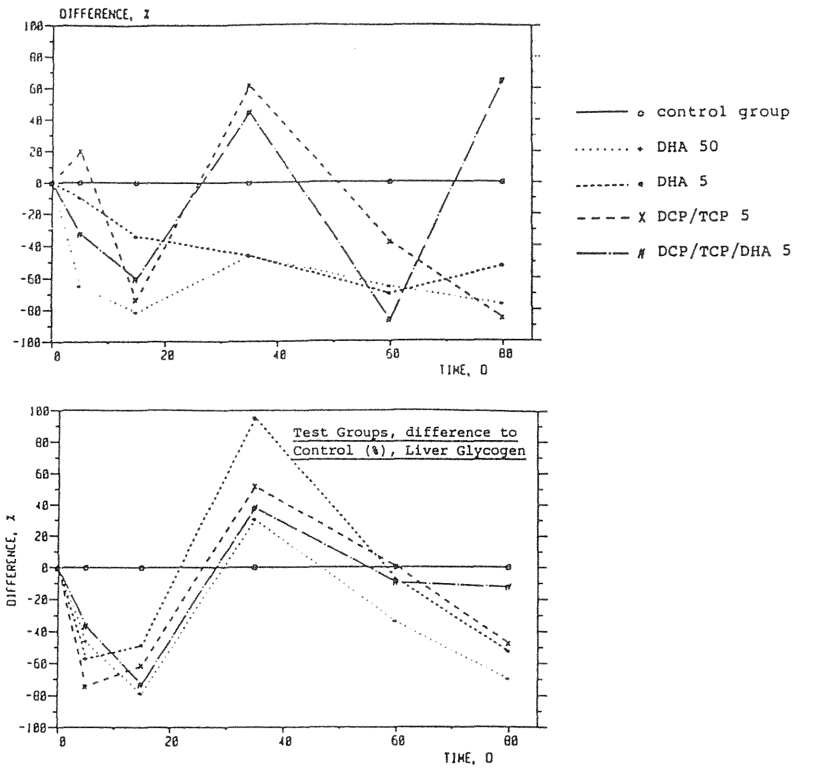


Figure 13. The difference in liver UDP-GT (A) and glycogen (B) concentration between test groups and the control group during exposure to DHAA (50 and 5 µg/l); DCP/TCP (5 µg/l); DCP/TCP/DHAA (5 µg/l) (Source: Tana 1988).

tions of chlorinated phenols stayed at the same level (below 1µg/l) and the resin acid concentrations varied between 1–2 µg/l (Tana & Lehtinen 1995).

4.3.5 Sterols

The observed effect on growth of fish exposed to bleached kraft pulp mill effluents cannot be explained by any organochlorine compounds, because the effect is independent of the AOX level of the effluent (Lehtinen 1990). They are presumambly caused by metabolic disturbances, possibly at the hormone level, because the cholesterol level of fish liver was increased in disturbed fish. Resin acids or chlorophenol conjugates did not correlate with the observed effects either, so speculations are now that sterols present in wood extractives contribute to these effects, although no conclusive evidence has been presented.

Plant sterols are well known to the pharmaceutical industry, e.g. ß-sitosterol and sitostanol are known to impede the intestinal absorption of cholesterol in humans (Heinemann et al. 1991). Although this is no proof of any adverse effects from sterols, it is an indication that they belong to a group of biologically active compounds. However, the physiological responses of fishes exposed in mesocosms to whole mill effluents were the same as for fish additionally exposed to sitosterol. The waterborne exposure experiments with fis also have showed that ß-sitosterol in the water can enter fish and consequently have reproductive effects suggesting a possible role in effecting reproductive changes in BKME-exposed fish (Maclatchy & van der Kraak 1994). Therefore, the effect levels of plant sterols in fish needs further clarification.

5 Biological effects of pulp mill effluents as a function of technical development

Extension of effect in time and space are the basic criteria for classification of environmental effects of all kinds of water pollution. The sum of effects which is causing irreversible changes in the aquatic ecosystem should be considered as more serious than those causing reversible damages, and effects in a vast area should be regarded as more serious than those affecting a smaller area. A scheme of classification of adverse effects in the aquatic ecosystem according to these criteria was proposed by Landner (see e.g. Lindeström et al. 1981). This scheme, originally developed for assessment of the various effects caused by discharges from conventional pulp mills, is shown in Table 8.

Table 8. Distribution of effects in time and space of adverse effects in the aquatic ecosystem caused by conventional pulp mill effluents. (Source: Lindeström et al. 1981)

Time	Short Term	Intermediate Effects; Reversible Effects	Long Term or Irreversible Effects
Local	• Death (fish, plankton) • Decreased light transmission (plants) • Avoidance reactions (fish) • pH-change (fish) • Oxygen deficiency in water mass (fish) • Growth stimulation (heterotrophic organisms)	• Accumulation of toxic substances (fish , molluscs) • Bad taste (fish, molluscs) • pH-change (benthic animals) • Oxygen deficiency in sediment-water-interface (benthic animals)	• Sedimentation of solids, i.e. fibres (benthic animals) • Formation of hydrogen sulphide (benthic animals) • Destruction of fish spawning grounds
Distant		• Decreased light transmission (plants) • Hampering of photosynthesis (algae) • Avoidance reactions (fish)	• Accumulation of toxic substances (fish, shellfish) • Bad taste (fish, molluscs) • Growth stimulation (algae) • Persistent genotoxic substances in drinking water (higher animals) • Disturbance of reproduction success (fish)

The local area may be defined as having a water mass of relatively high flush rate and the average residence time for refractory compounds is no longer than 10 days. Residence time for sediments is more than 12 months. The distant area may be defined as having a longer residence time of its water mass, up to several years, and is equal to the area where any effect can be detected. Short-term effects are reversible within weeks, intermediate effects within 12 months, and long-term effects are irreversible for more than a year.

Although a large fraction of the substances of an industrial effluent may decompose easily (illustrated by BOD7) and, therefore, influence only a local area of the receiving waters, there may still be a significant number of slowly degradable and possibly toxic compounds present, with the potential of expressing effects in a distant area. Ecotoxicological testing of samples of industrial effluents should , therefore, include biossays on both non-stabilized and aerobically stabilized samples (Folke et al. 1993b).

Potential short-term (direct exposure) toxic effects in the receiving waters caused by discharges of substances should be focussed on in the biotests using non-stabilized samples of waste water. Examples of substances causing these local-area effects are the ones with high acute toxicity, the ones with light-adsorbing properties, the ones causing avoidance reactions, pH-changes, or oxygen depletion, or the ones stimulating heterotrophic growth.

Long-term sublethal and chronic effects should be revealed by bioassays on samples containing only slowly biodegradable substances, i.e. in aerobically stabilized samples. Examples of substances causing these distant area effects are fibres and other settleable matter, bioaccumulating substances (especially if these exert chronic toxicity), off-taint or eutrophication causing substances, or persistent substances with genotoxic or other chronic toxic effects.

5.1 Single-species short-term toxicity

The, by now, classic review by McLeay (1987) covers the literature on aquatic toxicity of pulp and paper mill effluents until about 1987, i.e. mainly effluents from mills applying the 1970–1980 technical levels. A review by Bonsor et al. (1988) to some degree covers the technical developments including oxygen delignification of kraft pulp.

The acute lethal toxicity data on rainbow trout compiled by McLeay (1987) invariably showed acute toxicity of untreated effluents from production of both bleached and unbleached kraft pulp (as well as from other types of pulp production, sulphite, mechanical, chemo-thermomechanical). The acute 96h LC50-values of untreated effluents (unbleached and bleached kraft) varied between 3–65 % v/v and 5–87 % v/v respectively. Corresponding values for secondary treated effluents varied between 13 and > 100 % v/v for both categories of pulp production. The data are based on work by Fisher (1982), Loch & MacLeod (1973), Leach & Chung (1980), Holmbom & Lehtinen (1980), Miettinen et al. (1982), Nikunen (1983).

A compilation of effects, other than death, at acute exposure to bleached and unbleached kraft mill effluents carried out by McLeay (1987) reveals a wide range wherein effects occurred. The parameters used in studies of sublethal effects include effects on histology (fish), abnormal development of oyster larvae, metabolic stress in fish, effects on respiration and circulation in fish, effects on fish larvae, avoidance/attraction reactions in fish, and primary productivity of algae. The effect range for untreated, unbleached kraft pulp mill effluents was 1–>30 % v/v effluent dilution.

Primary treated bleached kraft mill effluents were tested for totally 24 different responses and showed median effective concentration ranges between 0.001 and < 40 % v/v effluent concentrations. The most sensitive reponses occurred in avoidance reactions to effluents by fish. Effects on algae occurred in a narrow concentration interval, i.e. between 3 and 10 % v/v (Eloranta et al. 1984; Nikunen 1983).

Secondary treated bleached kraft mill effluent toxicity varied between 0.1 and > 100 % v/v effluent dilutions. Responses of algae were the most sensitive parameter (Nikunen 1983; Anon. 1982). A thorough analysis of the reasons behind the large interval in effective dilutions of secondary treated effluents is not possible due to the fact that mill data on water consumption per ton pulp, or comparable information, were not given. During the period covered by McLeay (1987) the water consumption was highly varying between mills, especially between mills at different continents. Another fact is that the array of biological levels tested was large, from population levels (algae), whole-organism levels, to within-organism levels. This is further complicating a comparison. The impression is, however, that untreated unbleached and bleached kraft mill effluents had the same range of effective dilutions.

A series of medium-term laboratory tests for sub-acute effects in zebra fish and Ceriodaphnia were carried out, where the "Lowest Observed Effect Concentration" (LOEC) was determined for two endpoints:

A. Reproduction and survival of embryo/larvae

B. Induction of adverse effects during gametogenesis in fish, determined as reduced stress tolerance in the offspring (Landner et al. 1985; Neilson et al. 1990).

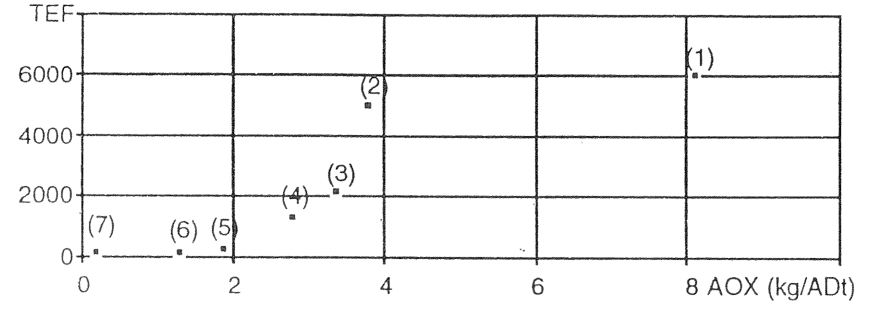
Based on data from such tests a relationship between AOX and Toxicity Emission Factor (TEF_{SA}) was determined for end-point B and is presented in Figure 14. As TEF often refers to acute lethality the subscript, SA=sub-acute, is used in Figure 14.

i) The amount of sub-acute toxicity, expressed as TEF_{SA} (TEF_{SA} = 100/LOEC x waste water flow per ton of pulp) for a mill using a conventional bleaching sequence, typical for the years before 1980, is about 1 000 for end-point A and 6 000 for end-point B. This serves as a reference for the worst case (End-point A not shown in the Figure).

ii) Introducing oxygen delignification without any other major change in the bleaching sequence will reduce TEF_{SA}-values to 500 (A) (not shown) and 5 000 (B). This is typical technology for the years around 1985 in Sweden and is becoming widespread in the USA.

iii) Reduction of the washing loss and carry-over of substance from the oxygen stage to the chlorination stage and better control of the bleaching process, including oxygen reinforcement of the extraction stage (Swedish mills at the end of 1980s), reduce the TEF_{SA}-value for one of the end-points (B) to about 2 100 but do not change TEF_{SA} for (A) (not shown in figure).

iv) The best available bleaching technology used in Sweden at the beginning of the 1990s, with oxygen delignification, followed by high chlorine charge (70 % of the active chlorine in the chlorination stage) produces an effluent giving sub-acute TEF-values of 170 (A) (not shown) and 250 (B), respectively.



(1) $C_{95}D_5$ Conventional Bleaching (<1980)
(2) O ($C_{85}D_{15}$) (1985)
(3) O $C_{92}D_8$ E(O) (End of 80s)
(4) O $C_{85}D_{15}$ + ASB
(5) O $C_{70}D_{30}$ (Last Generation)
(6) O $C_{70}D_{30}$ (Last Generation) + ASB
(7) O P D (Modern Fluff Pulp)

Mills and years refer to the Swedish situation

Figure 14. Relationship between AOX and Toxicity Emission Factor (TEF_{SA}) determined for reduced stress tolerance in fish offspring.

v) External treatment of the effluents in an aerated stabilization lagoon with a retention time of 8–9 days and which was operated with an an-oxic pre-zone for chlorate elimination, resulted in efficient reduction of most pollutants (Haglind et al. 1991). Furthermore, it was found that, irrespectively of the level of sophistication of washing and bleaching technology, the treatment decreased TEF-values two to four times. However, the reduction of AOX as a result of external treatment was normally around 30–40 %., to be compared with the drastic reduction in toxicity.

vi) Compared with the externally treated effluents (aerated stabilization lagoon) from mills using the "last generation" cooking, washing and bleaching technology, but still keeping a low degree of chlorine dioxide substitution (about 30 % of the active chlorine in the chlorination stage as D), giving an AOX in the treated effluent of 1.3 kg/ADt, bleaching sequences with 100% substitution and AOX-levels of 0.1–0.2 kg/ADt do not further reduce sub-acute TEF-values (Brunsvik et al. 1991;Haglind et al. 1991).

Toxicity Emission Factors (TEF) are frequently used to compare the toxicity of two different effluents: TEF=TU x Q, where Toxic Unit is definied as $100/EC_{50}$, and Q is the amount of process water discharged per tonne of pulp produced. When two pulp mill effluents are compared, clearly, the one with the highest TEF is more toxic. The question is, however, if a mill discharging a TEF of 400 is twice as toxic as one discharging a TEF of 200? Biological data are essentially logarithmic, e.g. decibel and toxicity data are normally attributed an exponential distribution. Then, in a LOGIT or PROBIT analysis the LOG EC_{50} value is used. Therefore, it may be more correct to use the formula

$$\log TEF = Q \times \log TU$$

as the basis for comparing two effluents. In this way log TEF = 0, if the effluent is non-toxic. After recalculation of data presented in Figure 14 the relationship of EOCl and toxicity, using the log TEF, to AOX is presented in Figure 15.

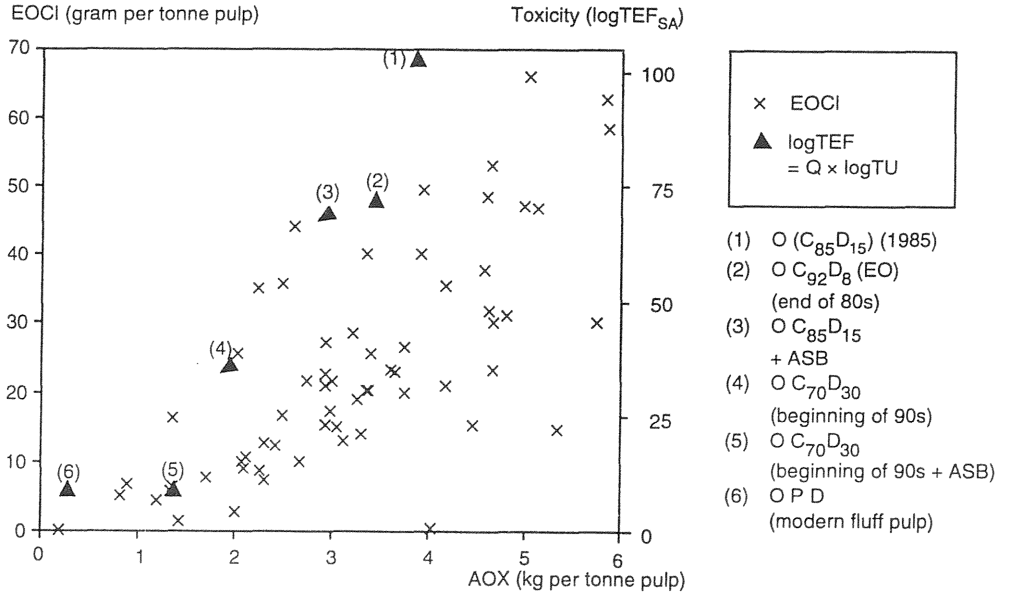


Figure 15. EOCl and sub-acute toxicity relationship to AOX. (Source: Folke et al. 1993a.)

The Figure 15 clearly shows that efforts to lower AOX discharges below approximately 1.2 kg/ADt do not reduce toxicity any further. However, it does not show whether the relationship between AOX and toxicity is an independent one, or whether it depends on the reduction of other compounds in the effluent (Folke & Renberg 1994).

Data are sofar scarce regarding toxicity comparisons between ECF and TCF pulp bleaching practices. Some results were recently published by Lövblad & Malmström (1994). Their data were recalculated on a logTEF basis by Folke & Renberg (1994) (Table 9). As mentioned, non-toxic effluents have a value of zero, as opposed to the traditional TEF value that for a non-toxic effluent would be equal to the specific water flow per ton pulp.

Table 9. Summary of logTEF data for primary treated whole mill effluents from ECF and TCF softwood (SW) and hardwood (HW) pulp production. (Source: Folke & Renberg 1994).

Mill	Sample	Microtox® bacteria sub-lethal toxicity	Selenastrum growth inhibition	Zebra fish reproduction	Ceriodaphnia acute tox & reproduction
Värö					
	SW ECF-1	15	0		
	SW ECF-2			24	
	SW ECF-3				0
Värö					
	SW TCF-1		0		
	SW TCF-2	5.3		3.7	
	SW TCF-3				0
Mönsterås					
	HW TCF-1	12	9.5		
	HW TCF-2			2.5	
	HW TCF-3				0

The data analysis indicates that a slight toxicity may be found in some bioassays for both ECF and TCF pulp. As long as the spent bleach liquors are discharged to the environment from both the ECF and TCF processes, it cannot be concluded on the basis of results in Table 10 that one bleaching technology is superior to the other in terms of single-species short-term toxicity.

In a study by Priha (1995, in press) the total effluents from all 15 Finnish pulp mills (Table 10) were tested with five laboratory-scale short-term toxicity tests. The tests were: immobilisation of *Daphnia*, luminescent bacteria test, growth inhibition/stimulation of green alga, early life stage development of zebra fish and MFO-activity in rainbow trout isolated hepatocyte culture.

The biological responses of the effluents are summed up in a frequency block chart (Figure 16). According to Priha (1995, in press) the figure does not show the rate of the impact, but only the different types of responses on a yes/no scale. In general the biologically treated bleached kraft mill effluents showed little or no toxicity regardless of bleaching technology (Figure 16). The mechanically treated effluents 14 and 15 showed the most frequent responses. Effluent 15 was from unbleached kraft production. The common characteristics for the effluents were that none caused *Daphnia* toxicity and all stimulated algal growth at some concentration (Priha 1995, in press). None of the secondary treated effluents at 100 % concentration affected the survival of zebra fish embryos and larvae, whereas the mechanically treated effluents were toxic. Only two of the effluents, both including effluents from TCF production, caused a slight induction in EROD activity. Seven of the effluents tested inhibited the EROD activity.

Table 10. Process and effluent characteristics of the pulp mills studied. Abbreviations: ECF (Elemental Chlorine Free), TCF (Totally Chlorine Free), CONV (D/C-stage bleaching), SW (Softwood) HW (Hardwood), AL (Aerated Lagoon), AS (Activated Sludge), MECH (clarifier and/or settling basin), BK (Bleached Kraft), UBK (Unbleached Kraft), SAP (Semialcaline pulp), (int) (integrated with paper and/or board production, indicated if joint effluent treatment) (Source: Priha 1995, in press).

Mill / sample no.	Bleaching type	Wood furnish	Effluent treatment	Production	Chemical characteristics of the whole-mill effluents BOD7 mg/l	COD Cr mg/l	SS mg/l	Tot.P mg/l	Tot.N mg/l	AOX mg/l
1	ECF	SW+HW	AL	BK (int.)	54	452	92	1.1	8.6	3.4
2	ECF	SW+HW	AL	BK	56	586	52	0.7	8.1	3.3
3	ECF	SW+HW	AL	BK	83	500	25	0.6	4.9	0.8
4	ECF	SW+HW	AS	BK	32	596	32	0.4	2.8	7.4
5	ECF	SW+HW	AS	BK	35	470	39	0.9	4.0	4.5
6	ECF	SW+HW	AS	BK	6	316	6	0.1	0.6	2.7
7	ECF	SW+HW	AS	BK (int.)	8	460	16	0.5	1.8	5.7
8	ECF	SW+HW	AS	BK	58	802	61	1.3	4.5	10.2
9	ECF+TCF	SW	AS	BK (int.)	12	233	34	0.2	3.7	2.1
10	ECF+TCF	SW+HW	AS	BK+UBK (int.)	16	250	11	0.3	1.8	1.2
11	ECF	SW+HW	AS	BK+UBK	5	410	8	0.7	6.1	6.7
12	ECF+CONV	SW+HW	AS	BK (int.)	10	464	66	0.3	3.0	10.4
13	CONV	SW+HW	AS	BK (int.)	16	738	51	1.3	13.1	12.0
14	ECF	SW	MECH	BK	155	568	22	0.3	2.6	-
15	-	-	MECH	UBK+SAP (int.)	335	783	72	0.9	5.7	-

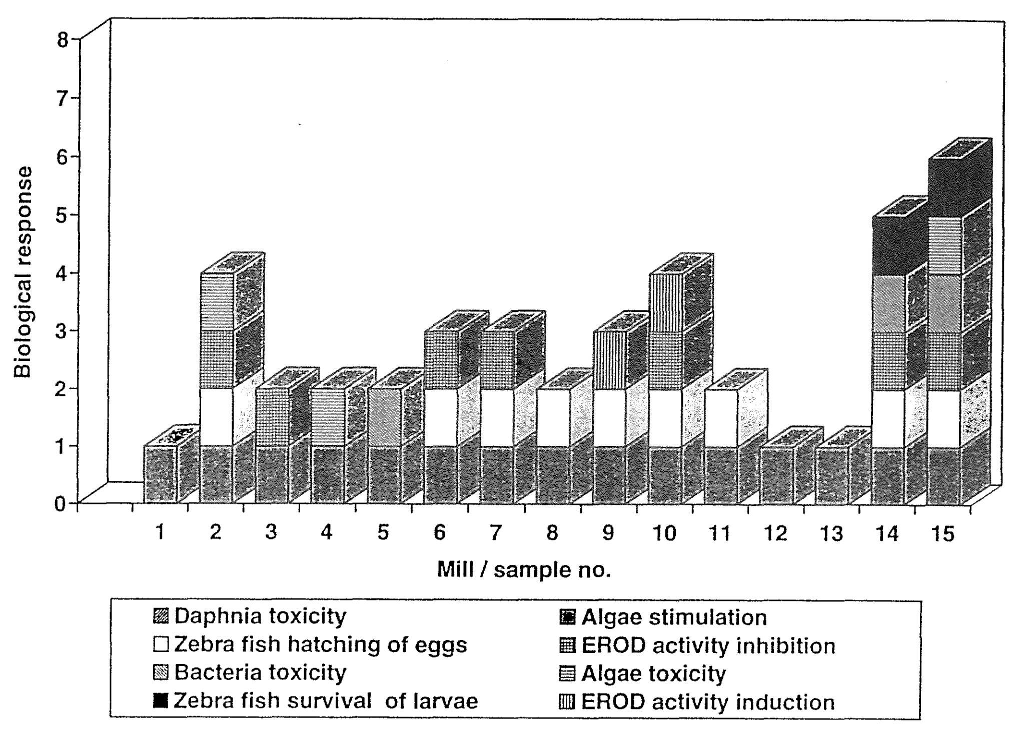


Figure 16. Frequency block chart of the different biological responses to the whole mill effluent exposures in laboratory tests. A missing block indicates "no-observed-effect". The height of the block does not indicate the strength of the observed effect. Numbers refer to the mills described in Table 10. (Source: Priha 1995, in press)

Verta et al. (1994) performed a series of short-term tests including algae growth inhibition test, luminescent bacteria test, *Daphnia* mobility inhibition tests and zebra fish hatching and survival test. Different effluents originating from production of soft- and hardwood ECF and TCF bleached pulp at two different mills were tested. Effluents were sampled from the bleach plant and from the total discharge after the treatment plant. Moreover, since ECF and TCF effluents were mixed at one of the mills, the bleach plant effluents were treated in a pilot activated sludge treatment plant. At the other mill, total effluents after the stabilization lagoon and after secondary treatment, were sampled.

The results from the different tests were summarized as a toxicity index. The calculation of toxicity index is presented in Verta et al. (1994). The toxicity indices obtained are presented in Table 11. It must be pointed out that the indices refer to effluents both from softwood and hardwood pulp production.

Table 11. Toxicity indices of effluents from production of conventionally bleached, and ECF and TCF bleached kraft pulp. (Source: Verta et al. 1994).

Effluent	Toxicity index	variation
Conventional, bleach plant,SW	0.88	
ECF,bleach plant,SW+HW	0.67	(0.50-0.88)
TCF, bleach plant,SW+HW	0.63	(0.56-0.69)
ECF,bleach plant, pilot treated,HW	0.19	
TCF,bleach plant, pilot treated,HW	0.13	
ECF/TCF,whole mill,SW+HW activated sludge treated,	0.02	(0.00-0.13)

SW = softwood; HW = hardwood

There were no significant differences in toxicity between ECF and TCF bleach plant effluents. The authors concluded that the toxicity generally was best explained by the COD content, phenolic compounds and by the content of resin and fatty acids. AOX did not correlate with toxicity. As in most studies in the literature, the water use per ton pulp was not considered, making a straight comparison with the results reported by, for example Folke & Renberg (1994), difficult.

Parallell with the study by Verta et al. (1994) as short-term toxicity study was performed by Kovacs et al. (1995) using the same untreated and pilot plant treated bleach plant effluents from hardwood pulp production as Verta et al. (1994) used in their biotests.

The battery of biotests used by Kovacs et al. (1995, in press) consisted of fathead minnow (survival, growth), Ceriodaphnia (survival, reproduction), Selenastrum (growth), and sea urchin (egg fertilization) tests. The effluent concentration causing a 25 % reduction in a particular endpoint (i.e. IC25) and its 95 % confidence interval was estimated. In addition, the effluents potential to cause hepatic MFO induction in rainbow trout was assessed by a means of a laboratory tets described earlier (Martel et al. 1994). The effluents were extensively chemically characterized. The results from the biotests are shown in Table 12.

Table 12. Results from biotests with untreated and secondary treated (pilot plant) hardwood bleach plant effluents (Source: Kovacs et al. 1995).

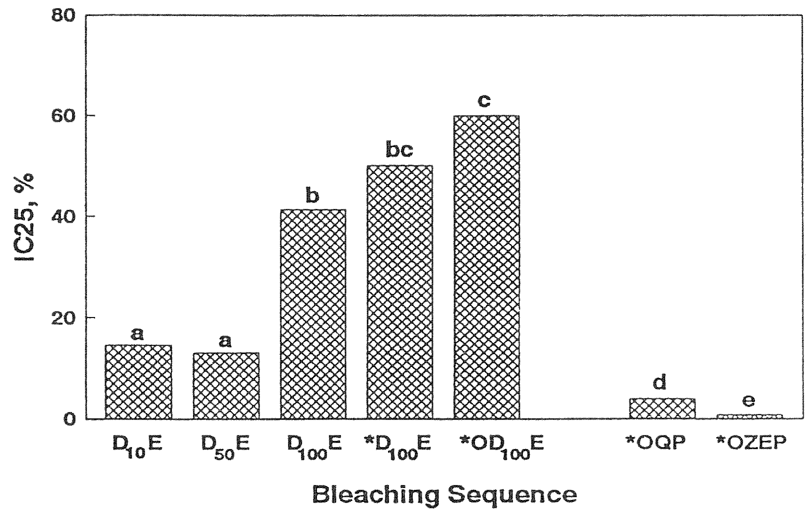
Effluent Sample	Fathead Minnow Survival/ Growth 7-d IC25, %	*Ceriodaphnia* Survival/ Reproduction 7-d IC25, %	*Selenastrum* Growth 4-d IC25, %	Sea Urchin Fertilization IC25, %	Rainbow Trout Hepatic EROD 4-d R.I.
Untreated ECF effluent	18 (11-22)[a]	13 (4-16)[a]	5.4 (2.7-6.6)[a]	8.6 (8-9.1)[a]	10.1*
Secondary-treated ECF effluent	57 (31-71)[b]	45 (41-52)[b]	21 (19-23)[b]	7.1 (6.2-7.8)[b]	8.6*
Untreated TCF effluent	28 (20-30)[c]	25 (1-35)[c]	16 (NC)[b]	6.4 (5.4-7.8)[b]	5.0*
Secondary-treated TCF effluent	60 (52-69)[b]	49 (20-64)[b]	37 (31-39)[c]	> 100 (NC)[c]	1.3

Note: IC25s sharing the same letters for each column are not different in a statistically significant manner.
Numbers in parentheses represent 95% confidence intervals
RI = Relative induction
* = Statistically significant induction ($p < 0.05$)
NC = Not able to calculate 95% CI

The biological tests indicated that the effluents were not highly toxic (three quarters of the IC25s were ≥ 10% v/v) and that, overall, the secondary treated TCF effluent was the most benign. When making the comparison between secondary treated ECF and TCF effluents, there was no difference in the ability of the effluents to cause effects in the Ceriodaphnia and fathead minnow tests. In the algae, sea urchin and MFO tests, the TCF effluent was less potent. The reason behind the lack of response in the sea urchin test may be the lower content of high molecular weight lignin in the TCF effluent than in the ECF effluent (Sangfors et al. 1994). The effect on sea urchin egg fertilization has been traced to reactive aldehyde groups in a high molecular weight fraction (Higashi et al. 1992).

Comparing untreated ECF and TCF bleach plant effluents, the sea urchin and rainbow trout MFO assay did not appear to be substantially different, while the algae, minnow and Ceriodaphnia were found to be more sensitive to the ECF effluent. The results confirm previous findings (O'Connor et al. 1994; O'Connor et al. 1993) that the sensitivities of different organisms and endpoints varies with different effluents, supporting the need for a battery of laboratory tests when comparing effluent quality.

O'Connor et al. (1994) used two brownstock pulps for laboratory bleaching experiments and studied the effluent toxicity with a series of short-term toxicity. The one pulp (Pulp I) can be considered as representative of conventional pulping technology and the other pulp (Pulp II) as representative of an effectively operating extended delignification system. Six sequences, representing both chlorine-containing and totally chlorine free (TCF) sequences, were used for bleaching: $(C_{90}+D_{10})E$, $(D_{50}+C_{50})E$, $D_{100}E$, $OD_{100}E$, OQP and OZEP. Pulp I was bleached solely with chlorine-compound-containing sequences. Pulp II (asterisk in Figures 17–19) was bleached with a D100E sequence and as well was used for those bleaching sequences which included oxygen delignification step (OD_{100}, OQP and OZEP).



** denotes effluents prepared using oxygen-delignified pulp (Pulp II)*

Figure 17. Chronic toxicity of laboratory prepared bleaching effluents on Ceriodaphnia reproduction. Bars which exhibit different letters are statistically significant different ($P < 0.05$) from one another. The data have been normalized to a water usage of 55 m^3/t pulp. (Source: O'Connor et al. 1994)

The effluents derived from $(C_{90}+D_{10})E$ and $(D_{50}+C_{50})E$ bleaching sequences exhibited acute lethal toxicity of 55 and 65 %, respectively for fathead minnows and marginal toxicity (92 and 98 %, respectively) for *Ceriodaphnia*. The remaining effluents did not show any lethal toxicity to either fathead minnow or *Ceriodaphnia*.

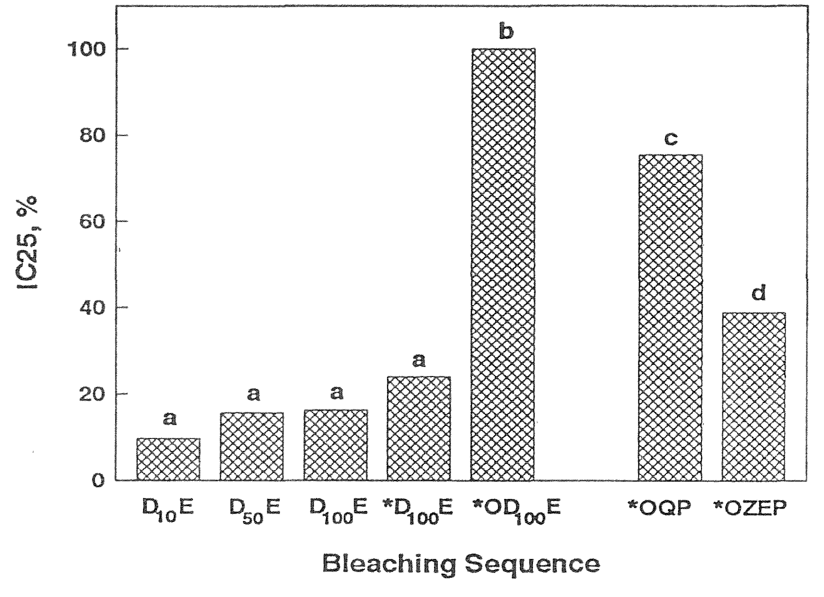
As shown in Figure 17 the effects of the various bleaching effluents on *Ceriodaphnia* reproduction followed the order: OZEP>OQP>$(C_{90}+D_{10})E$=$(D_{50}+C_{50})E$>$D_{100}E$>$OD_{100}E$. The effluent which produced the least chronic toxicity was the oxygendelignified pulp (Pulp II) bleached with 100 % ClO_2. The effluent from the pulps bleached using TCF conditions were exhibit the highest chronic toxicity to Ceriodaphnia (Figure 17).

In Figure 18 the effects on fathead minnow growth are presented. The effluent obtained from the bleaching of the oxygen-delignified pulp using 100 % ClO_2 did not exhibit any chronic toxicity to fathead minnows even when tested at full strenght (i.e. IC20>100 %).

In contrast to the results for *Ceriodaphnia* reproduction, the TCF effluents were less toxic than the effluents which were bleached with chlorine/chlorine dioxide (with the exception of the $OD_{100}E$ effluent).

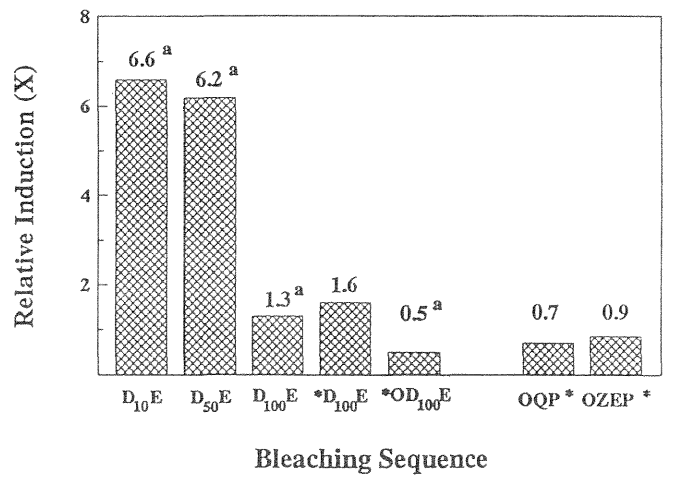
In the studies of O'Connor et al (1994) the mixed function oxidase (MFO) enzyme assays were also conducted. In these assays sexually immature rainbow trout were exposed to an effluent concentration of 2.5 %. After a four days exposure the activity of MFO enzyme EROD was analyzed. The results from these assays are presented in Figure 19.

As shown in Figure 19 the only effluents found to significantly induce EROD were those prepared using $(C_{90}+D_{10})E$ and $(D_{50}+C_{50})E$ and one of the two $D_{100}E$ bleaching sequences. The effluent from the $OD_{100}E$ bleaching sequence showed a significant inhibition in EROD response. The remaining effluents using TCF sequences did not significantly alter hepatic MFO activity.



** denotes effluents prepared using oxygen-delignified pulp (Pulp II)*

Figure 18. Chronic toxicity of laboratory prepared bleaching effluents on fathead minnow growth. Explanations same as in figure 17. (Source: O'Connor et al. 1994)



** denotes effluents prepared using oxygen-delignified pulp (Pulp II)*

Figure 19. Relative MFO enzyme induction, as measured by EROD assay, for rainbow trout exposed to laboratory prepared bleaching effluents at 2.5 % concentration for four days. "a" stands for bleaching effluents with statistically significantly higher activity than in controls. (Source: O'Connor et al. 1994)

O'Connor et al. (1994) compared the results from this laboratory-scale study to similar data from mill-scale bleaching trials. This comparison left the questions regarding the role of bleach plant effluent towards the acute/chronic toxicity and the elevation of MFO enzyme activity of whole mill effluents. For the chronic sublethal effects studied whether the bleaching was performed with chlorine-containing compounds or under TCF conditions, the least toxic effluent on a consistent basis was that bleached with the $OD_{100}E$ sequence.

In another study the EROD activity was measured in fingerling rainbow trout after a 96 h exposure to sublethal concentrations of 12 pulp and paper mill effluents (Gagne & Blaise 1993). Barring one primary-treated effluent where EROD activities were significantly depressed and two secondary treated effluents where no EROD induction were observed, all other effluents triggered significant induction of EROD, regardless of mill process/treatment or effluent lethality and chemical characteristics. This together wth results from the work of O'Connor et al. (1994) shows that practically any effluent may cause changes in the MFO-activity.

5.2 Effects of prolonged exposure on single -species

A relatively large number of laboratory studies have been conducted in Scandinavia and North America to determine the effects of pulp mill effluents on the organism level (whole-organism and within-organism level) (McLeay 1987; Lehtinen 1995, in press; Owens 1991; Solomon et al. 1993). The experiments have not been coordinated, so species, test system and measured end-points vary between experiments. In addition, the mill process, internal water use per ton of product are seldom or never clearly definied.

A compilation of effective effluent dilutions causing responses on whole-organism and within-organism levels is presented in Table 13. The studies have been made with effluents from production of pulp (bleached and unbleached) using technologies from the 1970s and early 1980s (McLeay 1987). The compilation is based on material published by McLeay & Brown 1974; Whittle & Flood 1977; McLeay & Brown 1979; NCASI 1968,1973, 1982, 1983, 1984ab; Stoner & Livingston 1978; McLeay 1973; Lehtinen & Oikari 1980; Webb & Brett 1972; Warren et al. 1974; Lehtinen et al. 1984; Seim et al. 1977. Some of the data from NCASI were generated in outdoor artificial streams.

Table 13. Range of effective concentrations for various biological effects in organisms exposed for a prolonged period of time to effluents from different pulping processes (Source: McLeay 1987)

Process	Treatment	Dilution range (% v/v)	N
Unbleached kraft	untreated	2.0–5.0	2
Unbleached kraft	primary	0.5–>30	7
Unbleached kraft	secondary	1.0–>5.0	7
Bleached kraft	untreated	<1.0–10	2
Bleached kraft	primary	0.1–>25	15
Bleached kraft	secondary	1.0–91	16

N = number of studies

From the tabulation above it can be seen that considerable similarity in effective dilution ranges occurred between primary treated unbleached and bleached kraft pulp mill effluents. Secondary treatment of unbleached kraft pulp mill effluents had little impact on effective dilutions. Secondary treated bleached kraft pulp mill effluents showed a wide range of effective dilutions, from high (1.0 % v/v) to practically undiluted. A range of various whole-organism and within-organism varibles are included in these studies, which may be partly responsible for the variations found in effective effluent dilutions (Table 13). Large variations between mills in water use and in-process conditions are also very plausible contributions to the variations noted. In recent laboratory studies treated effluents from a mill using "low-chlorine" bleaching were observed to cause physiological responses in whitefish in exposure dilutions ranging between 1.3–7.0 % v/v (Soimasuo et al. 1995). These results, as compared to those presented in Table 13 give reason to cast doubt on the contribution of the bleaching process to the effects noted.

In the 1980s, the Swedish EPA-financed project "Environment-Cellulose" may be considered the triggering factor for a worldwide discussion on the role of chlorinated organics in bleached pulp mill effluents (Södergren et al. 1988). Within this project, some laboratory experiments were performed in parallel with field studies (Andersson et al. 1988; Härdig et al. 1988; Bengtsson et al. 1989). These studies involved physiological and biochemical responses in fish exposed to untreated mill effluents originating from a softwood and a hardwood line with the bleaching sequence O(C85+D15)EDED and (C35+D65)ED respectively. The average water use was 50 and 60 m^3 per ton pulp respectively and the tested concentrations were adjusted in order to account for differences in water use between effluent sampling occasions.

The most pronounced response, also verified in the field, was observed in the activity of MFO-associated hepatic transformation enzyme 7-ethoxyresorufin-O-deethylase (EROD). The softwood pulp line effluent and a mixture of softwood/hardwood effluent induced the activity whereas hardwood pulp effluent did not. The exposed fish showed higher liver (220–320 µg/g) EOCl-values than control fish (62 µg/g) on a fat weight basis. However, the values were similar to those obtained in fish exposed to unbleached pulp mill effluents (Hemming & Lehtinen 1988). No other specific compounds than chlorinated phenols in fish and undiluted effluents were reported, making a clear-cut correlation between compounds and effects impossible.

Bengtsson et al. (1989) exposed fish, fourhorn sculpin and bleak, to untreated whole mill effluents from production of (i) unbleached hardwood (ii) bleached hardwood with 100% D, (iii) bleached softwood with 48% D in the CD-stage and finally (iv) to externally treated whole mill effluent from softwood pulp production with C84+D16. The softwood and hardwood effluents originated from two different mills, the other producing softwood and the other hardwood pulp at the time of sampling. The biochemical composition of the fish vertebrae after exposure to the effluents was studied and Table 14 presents the number of vertebral characteristics deviating from control fish. The authors stressed a possible link between competition for ascorbic acid used for detoxification processes and ascorbic acid dependent cartilage synthesis.

Table 14. Number of statistically significantly deviating vertebral characteristics in fourhorn sculpin, Myoxocephalus quadricornis, and bleak, Alburnus alburnus, exposed for 4.5 months to different pulp mill effluents. Total number of parameters studied=13. Percentage given in parentheses. (Source: Bengtsson et al. 1989)

	(i)	(ii)	(iii)	(iv)
Fourhorn sculpin	8(62)	6(64)	9(69)	2(15)
Bleak	4(31)	3(23)	7(54)	1(8)

(i) = Unbleached hardwood, untreated;
(ii) = Bleached hardwood (D100), untreated
(iii) = Bleached softwood (D48), untreated;
(iv) = Bleached softwood (D16), external treatment

The data presented in table 14 suggest that digestion products from hardwood pulp production produces substances acting on vertebral structure and biochemical parameters. Further, the bleaching with chlorine dioxide may partly destroy such compounds or they do not enter the effluent from the bleach plant (Lehtinen 1995, in press). The effluents originated, however, from two different mills and therefore cannot fully be compared. The results from exposure to softwood pulp effluents cannot be compared directly with the results from the experiment with hardwood since no unbleached softwood alternative was tested. External treatment of the bleach plant effluent (iii) from the high elementary chlorine bleaching seems to eliminate compounds producing vertebral anomalies.

The effects observed in bleak were fewer but in the same direction: (i) produced effects in a higher number of parameters than (ii). (iii) produced the highest number of effects and (iv) the fewest.

In parallel with the "Environment-Cellulose" project Finnish scientists were conducting a number of laboratory tests in which effluents both from unbleached and bleached pulp production were studied (Oikari & Nakari 1982; Oikari et al. 1984a; Oikari & Niittylä 1985; Oikari et al. 1985a). These experiments were largely not accounted in the conclusive summary reports of the Swedish "Environment-Cellulose" project (Södergren 1988; Södergren 1993).

In the work by Oikari & Nakari (1982) it was shown that resin acids in a simulated (unbleached) kraft mill effluent caused liver dysfunction in rainbow trout. Subsequent work showed that resin acids (as well as chlorophenolics) are conjugated in the liver and excreted through the bile (Oikari et al. 1984b). Physiological effects under exposure to these compounds and in combination with chlorophenols were detected on several levels (hematology, energy metabolism and detoxification).

An interesting response was the prominent inhibition of the conjugation enzyme UDP-GT involved in detoxification processes. This inhibition occurred with unbleached effluent components present only and did not require presence of chlorinated phenols. Liver dysfunction was indicated simultaneously as detected by increased plasma bilirubin levels (Oikari et al. 1984b). Oikari et al. (1984a) further demonstrated that compounds from unbleached pulp production to a larger degree affected energy metabolism in rainbow trout than simulated kraft mill effluent with chlorophenols added. The results by Oikari et al. (1984a) with inhibition of the UDP-GT activity in rainbow trout were also reproduced by Tana (1988) using pure dehydroabietic acid (DHAA).

The stimulatory effect in the EROD enzyme activity observed in both laboratory studies and in the field within the "Environment-Cellulose" project caught much attention also in North America and elsewhere (Södergren 1991; Munkittrick et al. 1994; Servos et al. 1994; van den Heuvel 1994). Induction of this enzyme activity was considered a sensitive indicator for exposure to BKME. Although the enzyme responds to exposure to compounds such as chlorinated dioxins (Muir et al. 1990; Lindström-Seppä & Oikari 1989a), it was concluded at the first pulp bleaching symposium in Stockholm (Södergren 1991), that EROD induction in fish could not be regarded as a specific indicator for exposure to effluents from bleached kraft pulp production. Lehtinen (1995, in press) summarized the responses obtained on EROD and UDP-GT activities in fish liver and fish liver cell cultures exposed to various pulp mill effluents as well as fractions of different effluents (Table 15).

The results in Table 15 show that there is a lack of consistent inductive reponses of the enzyme(s) when the organism or other biological fractions are exposed to effluents from production of bleached pulp using chlorine. EROD was induced also when fish were exposed to unbleached kraft pulp mill effluent or to black liquor only. Inhibition of activities was also noted in several cases.

The question arising in this connection is whether or not induction of enzymes such as EROD and UDP-GT and effects on other metabolic parameters in the "historical" perspective were related to bleaching with chlorine? Undoubtedly effects occurred and still do occur in bleached kraft mill effluent receiving waters, and effects are also observed in laboratory experiments (Robinson et al. 1994; Munkittrick et al. 1994; Servos et al. 1994). The effects on enzyme biomarkers occur, however, both when the pollutant originates from chemical (sulphate, sulphite) or thermomechanical, or (treated/untreated) bleached or unbleached pulp (Gagne & Blaise 1993; Huuskonen 1994; Lindström-Seppä et al. 1992a; Pesonen & Andersson 1992; Servizi et al. 1993).

Another fact, making conclusions on the biological severity of enzyme responses difficult, is the varying direction of the response, i.e. induction or inhibition (Lehtinen 1990). From work by Råbergh et al. (1992), Pesonen & Andersson (1992), Tana (1988), Oikari et al. (1983) and Oikari & Nakari (1982), strong evidence is given that extractives such as resin acids are cytotoxic and enzyme inhibitors and that such respones would be expected in fish exposed to effluents containing dominating levels of extractives. The work by Pesonen & Andersson (1992) shows that low levels of a complex pollutant may induce hepatic MFO-enzymes. With increasing pollutant concentrations a successive inhibition is reached. The problem arising here is that a level where the enzyme activity is similar to the control is sometimes reached and may cause a false negative result (Jimenez et al. 1990). Jimenez et al. (1990) tested this hypothesis on fish by using a known hepatotoxin and a subsequent challenge of the fish with benzo-a-pyrene (BaP). The administration of the hepatotoxin significantly reduced the ability of the liver to induce the EROD activity as a result of BaP exposure.

The observations by Jimenez et al. (1990) are highly important for the interpretation of studies on pulp mill effluents, both in the laboratory and in the receiving waters. Low EROD or any other enxyme activity in exposed fish may indicate two things, i.e. absence of inducing substances or hepatotoxic levels of contaminants. Consequently, comparison of several biomarker responses is needed to provide information for correct interpretation of MFO responses. Such biomarkers would include general metabolic ones reflecting the nutritional status (liver glycogen, liver lipids etc.), histopathology and serum enzyme levels and biomarkers related to reproduction (Munkittrick et al. 1992). Finally, biomarkers have to have a defined linkage to the level of exposure in order to be useful- and need to be associated with particular chemicals or toxicity syndromes. Otherwise, the sig-

Table 15. Hepatic phase I, EROD abd phase II, UDP-GT enzyme responses in fish liver and liver cell cultures exposed to various pulp mill effluents.

Process/fraction	Treatment	EROD	UDP-GT	Species	Durationof exp.	Reference
O(C85+D15)	none	Induction	Induction	Perch	Norrsundet,field	Anderssonet al. 1988
CDEoDED	yes	Induction	N.A.	Rainbow trout	4 days	Martel et al. 1993
DEoDED	yes	Induction	N.A.	Rainbow trout	4 days	"
O(DC)EoDD	yes	Induction	N.A.	Rainbow trout	4 days	"
Unbl.KME	yes	Induction	N.A.	Rainbow trout	4 days	"
Blackliquor	none	Induction	N.A.	Rainbow trout	4 days	"
TMP	yes	No effect	N.A.	Rainbow trout	4 days	"
CTMP	yes	No effect	N.A.	Rainbow trout	4 days	"
TCF	yes	Induction	N.A.	Rainbow trout	4 days	"
Unbl.KME	yes	Inhibition	N.A.	Rainbow trout	18 days	Huuskonen1994
TMP	yes	No effect	Inhibition	Rainbow trout	8 weeks	Lehtinen et al. 1993
Sulphite mill extract	none	Inhibition	N.A.	Primarycell cult.	hrs	Pesonen 1992
KMEmill extract	none	Inhibition	N.A.	"	hrs	Pesonen 1992
BKME/KME	yes	Inhibition	N.A:	"	hrs	Hänninenet al.1991
Simulated KME	none	N.A.	Inhibition	Rainbow trout	11 days	Oikari& Nakari 1982
QeZ(Eop)ZEP	none	Inhibition	No effect	Rainbow trout	8 weeks	Sangforset al. 1994
"	yes	Inhibition	No effect	Rainbow trout	8 weeks	"
D(Eop)DED	none	No effect	No effect	Rainbow trout	8 weeks	"
"	yes	No effect	No effect	Rainbow trout	8 weeks	"

C=Chlorinegas; D=Chlorinedioxide;O=Oxygen stage; Z=ozone; Eop=Alcaline stage+oxygen and peroxide; Qe=Enzyme and chelating agent; TMP=Thermomechanical pulp; CTMP=Chemithermomechanical pulp;TCF=Totally chlorine free; KME=Kraft mill effluent nificance of any observation will be unknown and useless for directing technical changes in mill operations.

End-points with significance for the population such as reproduction under pro-longed exposure have not been studied with effluents originating from mills adopting bleaching technology of the 1990s. Such studies are important in the future, since effects on the reproductory system have been observed in recent Swedish and Canadian field studies outside mills employing both chlorine and non-chlorine bleaching practices (Sandström et al. 1988; McMaster et al. 1991; Munkittrick et al. 1991; Munkittrick et al. 1994).

Tana & Nikunen (1986) and Vuorinen & Vuorinen (1987) studied the hatchability of pike eggs and the effects on early life stages of brown trout, respectively, under exposure to BKME representing the bleaching technology of the 1980s. Tana & Nikunen (1986) found an increased egg survival in pike caught from the polluted water area as compared with eggs from unexposed parents. However, fry from exposed parents did not stand additional stress. The tested effluent dilutions were between 0.5 and 10 % v/v. In the work by Vuorinen & Vuorinen (1987) the eggs were fertilized in clean water and incubated in polluted water with effluent dilutions ranging from 0.5 to 2 % v/v. Thus, no comparison on acclimatory responses were made as in Tana & Nikunen (1986). Percentage hatching (2 % v/v) was lower than in controls. Newly hatched fry were smaller in all dilutions tested and the yolk absorption was retarded. Post-hatch exposure also retarded growth and devlopment of the fry. All sac fry died after 4 weeks of exposure in 2 % effluent concentration.

The results referred show that old technology BKMEs affected early life stages of fish. However, in neither study was it possible to relate the results to bleaching, since the effluents tested were whole mill effluents. In the study conducted by Vuorinen & Vuorinen (1987) the COD-values were rather high based on effluent concentration (1 200 mg/L) as compared with treated effluents from new technology mills with external treatment (400–500 mg/L) (Lehtinen et al. 1994). Thus, the role of other in-mill process streams to the effects noted cannot be excluded.

5.3 Effects of prolonged exposure in multi-species testing systems, model ecosystems

The biological effects of total pulp mill effluents from mills with different bleaching procedures have been systematically studied in model ecosystems along with the technical development since the beginning of the 1980s (Rosemarin et al. 1986; Lehtinen et al. 1988; Hemming & Lehtinen 1988; Lehtinen 1989; Lehtinen et al. 1990; Lehtinen 1990; Rosemarin et al. 1990a; Lehtinen et al. 1991; Lehtinen et. al. 1992; Lehtinen et al. 1993; Tana et al. 1994; Lehtinen et al. 1994).

Effects on both community and population level as well as on whole-organism and within-organism levels have been studied in this work. At the community level the main emphasis was in the beginning put on the community structure. From 1991 onwards, also functional mechanisms such as system carbon binding, consumption of carbon dioxide, oxygen production etc. have been studied. Effects on fish populations (growth, mortality) were studied using larvae of the three-spined stickleback, *Gasterosteus aculeatus*, and effects on whole- and within-organism level were studied using rainbow trout as test organism. The physiological test program has been modified during the work in accordance with experiences from earlier results. Generally, most of the responses measured are comparable between the years.

The results from tests performed during the period 1982–1985 have been summarized as effect factors by Lehtinen et al. (1991). The data were calculated as "effect factors" in order to obtain a common base for comparison of the different effluents. The basic material has been thoroughly evaluated and the intensity of an effect has been assigned a value on a scale between 0 and 5, where 0 = no significant deviation from the control and 5 = strongest observed effect. The mean value for all the parameters is referred as the calculated "Effect Factor".

The investigated parameters and the calculated "Effect factors" for four alternatives corresponding to different groups of parameters are listed in Table 16 and Table 17.

The effect factors for alternatives 1 and 3 (see Table 17) (with and without fish physiology and EOCl= Extractable Organic Chlorine) were plotted against the TOCL kg/t (Total Organic Chlorine) per ton pulp for the different effluents (Figure 20).

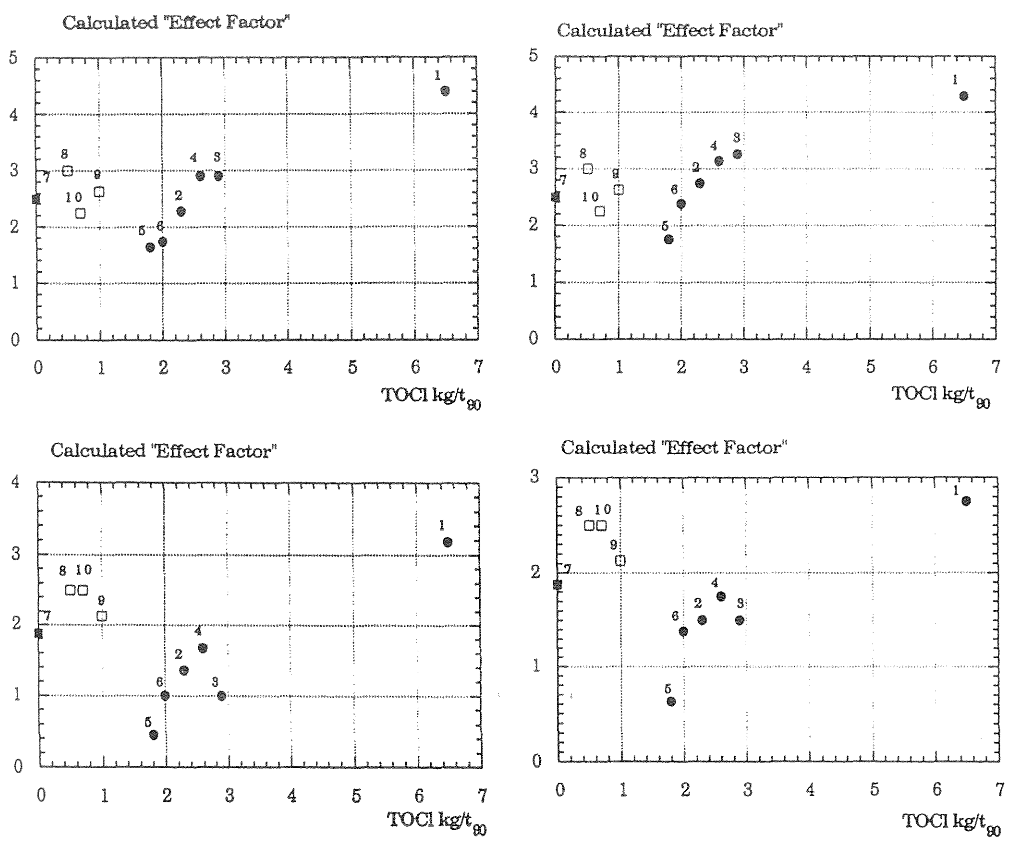
Table 16. Parameters studied in model ecosystem experiments during the period 1982–1985. (Source: Lehtinen et al. 1991)

Effluent no.	1	2	3	4	5	6	7	8	9	10
EOCl in fish and snails							x	x	x	x
1. Bladder wrack										
Biomass	x	x	x	x	x	x	x	x	x	x
Apical growth	x	x	x	x	x	x	x	x	x	x
2. Invertebrates macrofauna										
Biomass	x	x	x	x	x	x	x	x	x	x
Abundance	x	x	x	x	x	x	x	x	x	x
3. Fish, stickleback										
Mortality	x	x	x	x	x	x	x	x	x	x
Growth	x	x	x	x	x	x	x	x	x	x
Histology	x	x	x	x	x	x	x	x	x	x
Parasite frequency	x	x	x	x	x	x	x	x	x	x
4. Fish, rainbow trout										
Physiology	x	x	x	x	x	x				

Table 17. Calculated "Effect factors" for four alternatives corresponding to different sets of parameters investigated in the model ecosystems (Source: Lehtinen et al. 1991).

Effluent no.	Type of effluent	Calculated "Effect Factors"[a]							
		Alternative 1		Alternative 2		Alternative 3		Alternative 4	
		High dose	Low dose	High dose	Low dose	High dose	Low dose	High dose	Low dose
1	SW (C95 + D5)EHDED	4.40	3.18	4.63	3.33	4.29	2.75	4.60	3.67
2	SW (C87 + D13)EDED + AL[b]	2.27	1.36	2.33	1.33	2.75	1.50	3.00	1.50
3	SW O(C83 + D17)EDED	2.90	1.00	2.44	0.56	3.25	1.50	2.67	0.83
4	SW O(C85 + D15)EDED + pAL[b]	2.90	1.67	2.44	1.14	3.13	1.75	2.50	1.17
5	SW O(C84 + D16)EDED + ppAL[b]	1.63	0.45	1.33	0.22	1.75	0.63	1.33	0.33
6	SW O(C52 + D48)EDED	1.73	1.00	1.00	0.56	2.38	1.38	1.50	0.83
7	SW Unbleached	2.50	1.88	2.67	2.00	2.50	1.88	2.67	2.00
8	HW (D92 + C8)(E + P)D(E + P)D	3.00	2.50	2.50	2.17	3.00	2.50	2.50	2.17
9	HW O(C82 + D18)EDED	2.63	2.13	2.00	2.00	2.63	2.13	2.00	2.00
10	HW O(C51 + D49)EDED	2.25	2.50	1.50	2.17	2.25	2.50	1.50	2.17

[a] Alternative 1 All parameters investigated are included, except EOCl.
Alternative 2 Same as Alt. 1 but chlorate effects (biomass, apical growth) on bladder wrack excluded.
Alternative 3 Same as Alt. 1 but fish physiology excluded.
Alternative 4 Same as Alt. 1 but chlorate effects on bladder wrack, fish physiology and EOCl excluded.
[b] AL = Aerated lagoon. pAL = Partial aerated lagoon. ppAL = Pilot plant aerated lagoon.



Calculated "Effect Factors" for Alternative 1 (all parameters investigated, except EOCl) plotted against the TOCl-values for the respective total-mill effluents.

Lower part: low dose, 2000 times dilution
Upper part: high dose, 400 times dilution
● *bleached softwood kraft pulp*
■ *unbleached softwood kraft pulp*
□ *bleached hardwood kraft pulp*

Calculated "Effect Factors" for Alternative 3 (all parameters investigated, except EOCl and fish physiology) plotted against the TOCl-values for the respective total mill effluents.

Lower part: low dose, 2000 times dilution
Upper part: high dose, 400 times dilution
● *bleached softwood kraft pulp*
■ *unbleached softwood kraft pulp*
□ *bleached hardwood kraft pulp*

Figure 20. Calculated "Effect Factors" for alternative 1 and 3 from table 17. (Source: Lehtinen et al. 1991)

Following conclusions from the data in Figure 20 may be drawn:

- The TOCl-values correlate reasonably well with the "Effect Factors" obtained for bleached softwood kraft pulp.
- The effluent from production of *unbleached* softwood kraft pulp has a high effect factor despite a TOCl-level of zero.
- The bleached hardwood kraft pulp mill effluents show much higher effect factors than would be expected from softwood kraft pulp TOCl-relationship.

The results implied that no general conclusions on the environmental impact of an effluent can be made from its TOCl-content. It is also evident that other process internal factors and substances not included in the bleaching contribute to the effects noted.

To date, whole mill and bleach plant effluents from production of softwood and hardwood pulp have been studied in model ecosystems. The studies have also included effluents from unbleached and thermomechanical (TMP) pulp production. So far no pure paper mill effluents have been studied. The effluents from chemical pulp production cover the spectrum from conventional bleaching to ECF and TCF bleaching processes. The effluents tested in model ecosystems during the period 1982–1993 are presented in Table 18.

All effluents have been normalized to a water consumption of 50 m^3 per ton pulp. The effluent dilutions have always been 400–2 000 times except for in Tana et al. (1994) where the dilutions used were 200 and 1 000 times. Originally, the objective with the model ecosystem studies were to evaluate the ecosystem impact of whole mill effluents from mills employing new bleaching technologies, i.e. turning from conventional chlorine bleaching to oxygen delignification, higher use of chlorine dioxide instead of chlorine, low chlorine multiple bleaching etc. However, this approach does not permit comparison of the effect contribution from the different compartments of the mill, especially when it has not been possible always to compare the same mill at every experiment. In some instances the same mill has been compared (numbers 4 to 6 and 13,14 in Table 18). Despite this possibility, an evaluation of the significance of a general decrease of the organic matter content in the effluent at every technological level is not directly possible.

In order to compare the different effluents originating from processes with different technological levels some comparable structural effects are compiled in Figure 21. The numbers in Figure 21 refer to the processes numbered in Table 18.

Table 18. Pulp mill effluents tested in model ecosystems during the period 1982-1993. HW = hardwood; SW = softwood.

Process		Treatment	Year
1. SW (C95+D5)EHDED,	whole mill	none	1982
2. SW (C87+D13)EDED,	whole mill	aerated lagoon	1983
3. SW O(C83+D17)EDED,,	whole mill	none	1983
4. SW O(C84+D16)EDED,	whole mill	partial aeration	1983
5. SW O(C84+D16)EDED,	whole mill	aerated lagoon	1984
6. SW O(C52+D48)EDED,	whole mill	none	1984
7. SW O(C60+D40)(Eo)DED	bleach plant	none	1989
8. SW O(C60+D40)(Eo)DED	whole mill	none	1989
9. SW O(C85+D15)(Eo)DED	bleach plant	none	1989
10.SW OPD	bleach plant	none	1989
11.HW (D80+C20)(Eop)DED	whole mill	none	1990
12.HW (D80+C20)(Eop)DED	whole mill	aerated lagoon	1990
13.HW O(D27,C68+D5)(Eop)(Ep)D	whole mill	none	1990
14.HW O(D27,C68+D5)(Eop)(Ep)D	whole mill	aerated lagoon	1990
15.SW (C84+D16)(Eo)DED	whole mill	activated sludge	1991
16.SW TMP+newsprint	whole mill	aerated lagoon	1991
17. Phytosterols			1991
18.SW O(D91+C9)(Eo)DED	whole mill	activated sludge	1992
19.HW DEoDED	bleach plant	none	1993
20.HW/SW DEoDED	whole mill	none	1993
21.HW QeZEopAzEPA	bleach plant	none	1993
22.HW QeZEopAzEPA + SW DEoDED	whole mill	activated sludge	1993

HW = Hardwood; SW = Softwood

The responses presented in Figure 21 are given as per cent of the respective controls for different years, on bladder-wrack (Fucus) growth, sediment invertebrate abundance, Fucus associated invertebrate abundance, and total system abundance (incl. walls of the model ecosystems). The abundance of animals has been considered more important than biomass since the abundance of individuals better reflects the total genetic information available within the community. Effects on bladder-wrack growth is mostly an effect of chlorate.

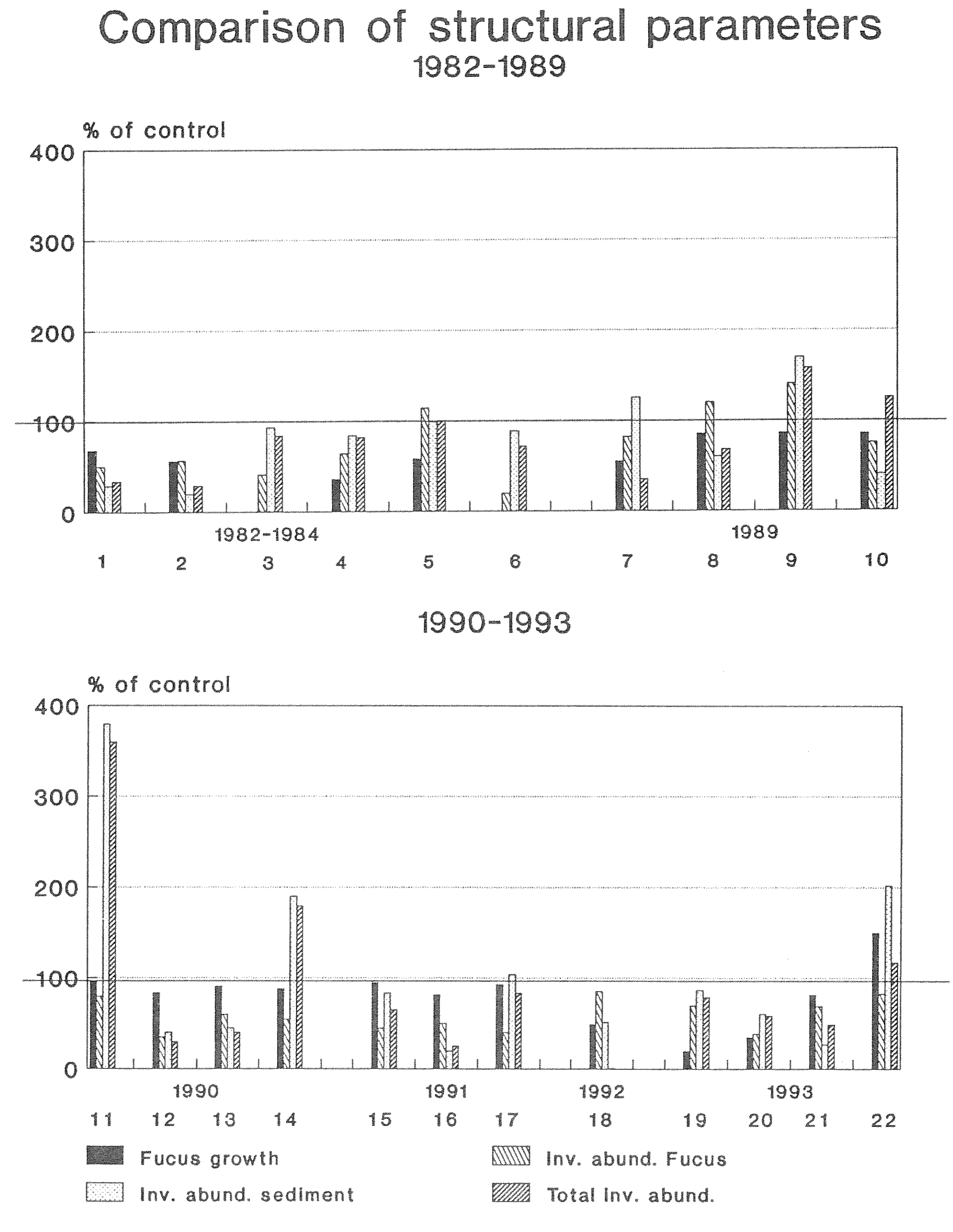


Figure 21. Structural responses in model ecosystems exposed in 400 times dilution to various pulp mill effluents.

From the Figure 21 it is seen that effluents 1 and 2 distinctly negatively affected all parameters. The effect was very much similar despite differences in TOCL, 6.5 and 2.4 kg/t, respectively. Interestingly, also phytosterols alone (no.17) affected bladder-wrack invertebrate abundance. Moreover, tertiary treated effluent from an integrated TMP-newsprint mill (No.16) affected the structural parameters in the same order as effluents 1 and 2. Effluents 19–21 (untreated bleach plant or untreated whole mill effluent) from ECF and TCF pulp bleaching inhibited invertebrate abundances. Activated sludge treatment of mixed ECF/TCF mill effluent was stimulatory. It may also be noted that untreated effluent (No 9) from a bleach plant with the sequence O(C85+D15)(Eo)DED also stimulated invertebrate abundances. Effluent No. 11 (D80+C20)(Eop)DED stimulated (eutrophication?) the abundance most. Aerated effluent 14 (low chlorine multiple bleaching) was also stimulatory for the invertebrates.

In conclusion, there was no relation between bleaching process and the outcome of the exposure on the invertebrate community. On the organism level the results based on 23–27 different physiological and morphometric parameters in rainbow trout, exposed to effluents simultaneously with the model ecosystem experiments from the period 1989–1993 have been compiled into reponse indices in Figure 22. The tested effluents are compared by giving each parameter a number between 0 and 5, where 0 = 0–10 % difference from control and 5 = over 50 % difference from control. The numbers are then added and thereafter divided by the number of parameters. In the response index both lower and higher values compared to control have been included. The effluent numbers in Figure 22 refer to numbers presented in Table 18.

Figure 22 reveals that ECF and TCF bleach plant effluents (No 19 and 21 in Fig.23) from 1993 are identical when it comes to physiological and morphometric responses in rainbowtrout. Untreated mixed hardwood/softwood whole mill effluent (No. 20) as well as treated ECF/TCF whole mill effluent (softwood +

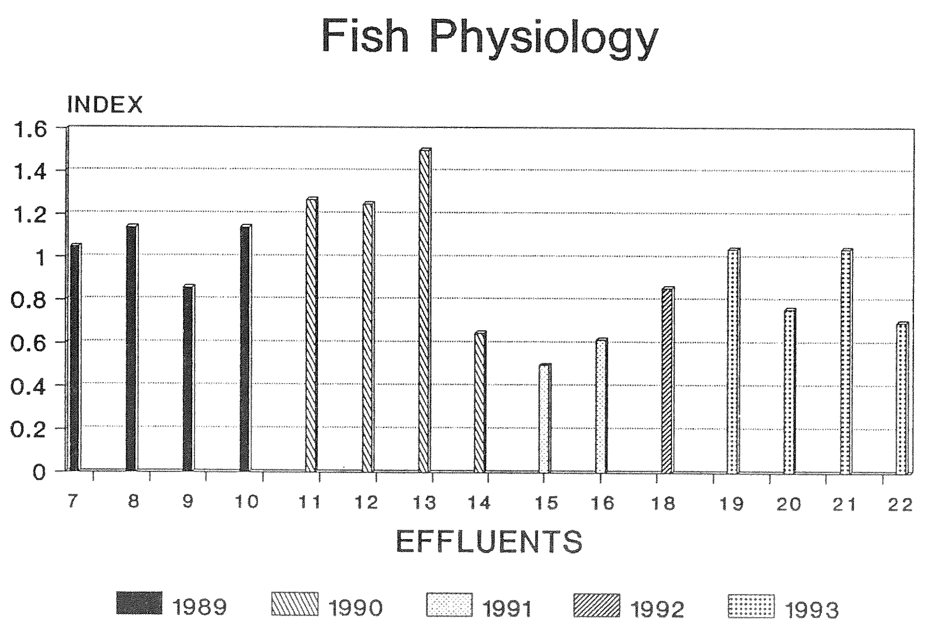


Figure 22. Response indices of rainbow trout exposed at 400 times diluted effluents from various pulp mill effluents in the period 1989–1993.

hardwood) caused some of the lowest impact on fish. Treated whole mill effluent from low chlorine multiple bleaching (No. 14) also had a low impact on fish. This was also the case with tertiary treated TMP-effluent. The lowest response index was calculated, however, for fish exposed to activated sludge treated whole mill effluent from a mill with conventional chlorine bleaching.Thus, also in the case with physiological responses on fish bleaching sequence per se was not the primary reason behind a high or low impact. Most probably in-mill process solutions, which vary from mill to mill, must be a major factor for the environmental impact from a modern mill.

Sangfors et al. (1994) made a similar compilation on response indices vs. COD based on whole ecosystem responses (Figure 23). In this case a better correlation between lower COD-discharge and lower impact indexes are observed. This may be expected, since other processes prevail in an ecosystem than within organisms. For example the quality of COD, including less biodegradable substances will influence upon heterotrophic activity, nutrients and organic carbon on both autotrophic and heterotrophic processes. In any case it is seen that mills applying technology of the 1990s produce effluents with a very low environmental impact regardless of whether bleaching is done with chlorine containing chemicals or not, as illustrated with the model ecosystem technique.

5.4 Field studies

Pulp mill effluents have a history associated with adverse effects in receiving waters. The large scale discharge of organic material and fiber from many pulp mills prior to 1970 was the primary cause of the observed environmental impacts.

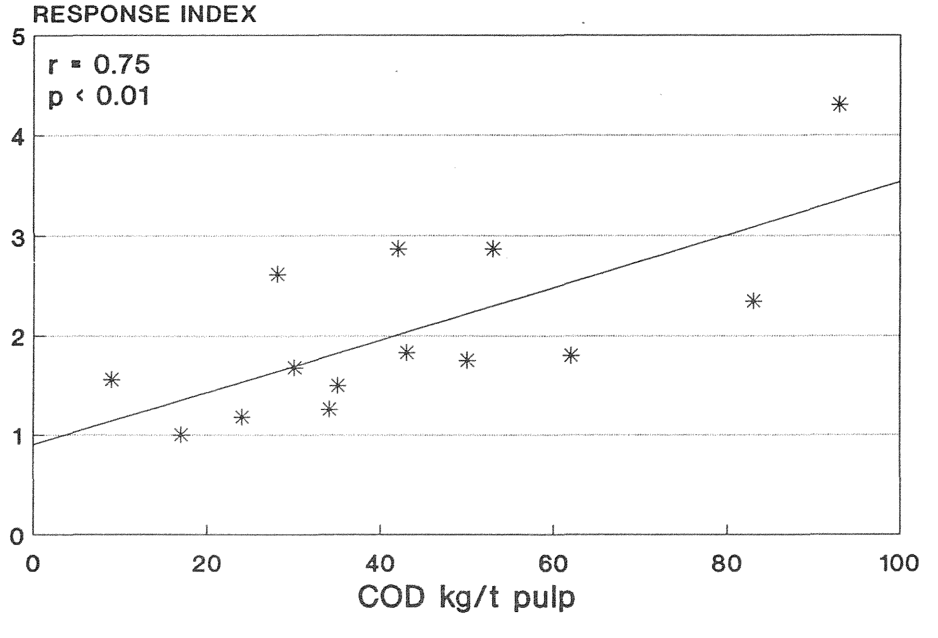


Figure 23. Ecosystem responses (including organism-levels) versus COD (kg/t pulp) after exposure to various pulp mill effluents. (Source: Sangfors et al. 1994)

In a review of studies up to the beginning of the 1980s on toxic effects of pulp mill effluents in receiving waters (McLeay 1987), it was concluded that the vast majority of receiving water studies conducted did not distinguish biological effects due to toxic constituents from those caused by other effluent characteristics. It was also concluded that very few of these receiving-water studies had attempted to define the toxic zone of influence caused by a mill discharge. The preponderance of receiving-water studies associated with pulp and paper mill discharges have examined biological changes in communities of benthic invertebrates, phytoplankton an periphyton. Although many site-specific effects have been demonstrated, few if any of these studies have shown that these changes resulted in adverse effects on fisheries resources. Instances, where significant environmental effects on aquatic life had been demonstrated, were normally associated with pulp and paper mills discharging untreated or primary-treated effluents into poorly flushed waters with limited capacities for dilution and dispersal. In the same review (McLeay 1987), no studies were found which could show conclusive evidence of significant toxic effects within receiving waters attributable to typical biotreated mill effluents. Application of the findings reviewed to other discharge situations were, in most instances, vitiated by lack of definition of effluent type, quality and treatment; effluent dispersal patterns and receiving-water concentrations; and/or the characteristics of the receiving waters.

5.4.1 Effects on primary production

Primary productivity studies have been shown to provide valuable information for assessing impacts of a variety of pollutants on aquatic ecosystems (Rodgers et al 1979, Amblard et al. 1991). However, very few studies have monitored the impact of mill waste on natural populations of primary producers (Stockner & Cliff 1976, Moore & Love 1977, Eloranta & Kettunen 1979, Eloranta & Eloranta 1980).

The few studies of kraft pulp mill effluents (KME) on primary production have attributed their respective results to one or more of three major sources: (1) light attenuation from color; (2) phytotoxicity; or (3) eutrophication. The concensus of conclusions based on these marine studies was that light attenuation was the overriding factor for decreases in natural phytoplankton photosynthesis (Parker & Sibert 1976, Stockener & Cliff 1976, Stockner & Costella 1976). The results from a study by Mechenich (1980) on the effect of color on phytoplankton in Lake DuBay, Wisconsin concur with the previous conclusions. Mechenich (1980) found that photosynthetic rates increased when lake water color was reduced, increasing light penetration. Different conclusions were presented by Moore & Love (1977), who tested KME effects on phytoplankton and periphyton populations in Nipigon Bay, Lake Superior. They determined that low concentrations of KME and low pH depressed photosynthesis due to toxic effects rather than light attenuation. The influence of secondary-treated kraft mill effluent (BKME) on periphyton caused a nutrient enhancement effect; i.e increased growth with increasing watewater concentration (Bothwell & Stockner 1980).

Available literature indicates that impacts on primary productivity by the pulp and paper industry are somewhat site-specific. Based on published data, one might expect that a secondary treatment systems lessen any potential toxic impact, and light-attenuations from BKME color may have more significant impacts. Secondary treatment does not completely remove effluent color since organic compounds responsible for coloring BKME, such as sulfonates and other wood extractives, are highly resistant to bacterial degradation (Wong & Prahaes 1977). Responses of periphyton and phytoplankton productivity in the lower Sulphur River (Texas-Arkansas) to secondary treated bleach kraft mill effluent were monitored (Davies et al. 1988). Periphyton productivity was not significantly decreased downstream of a mill discharge, nor were periphyton efficiences. The community structure of the periphyton community shifted towards heterotrophic populations near mill discharge but recovered to upstream characteristics at distant downstream stations.

Phytoplankton primary productivity and productivity efficiency were significantly decreased downstream of the mill discharge. These decreases were associated with increased light attenuation due to mill effluent. As chlorophyll-a concentrations of periphyton and phytoplankton were not significantly altered, the effluent was not concluded to be lethal to the algae. In lake mesocosm studies (Salkinoja-Salonen et al. 1993) secondary treated effluents did not show any destructive effects on lake water phytoplankton.

Kautsky (1992) reported clear impact on the ecosystem near outfalls of Iggesund and Norrsundet and in both cases bladder-wrack, *Fucus vesiculosus*, was most affected. It is unclear from the paper whether this could have been caused by chlorate. A more plausible explanation is that the inner fjords of Iggesund and Norrsundet have high color and little salinity due to fresh water input from the lakes and rivers. Bladder-wrack is a marine or brackish water organism. Low salinity water (below 4 o/oo) and high water color does not provide optimal growth for this species (Folke et al. 1993b).

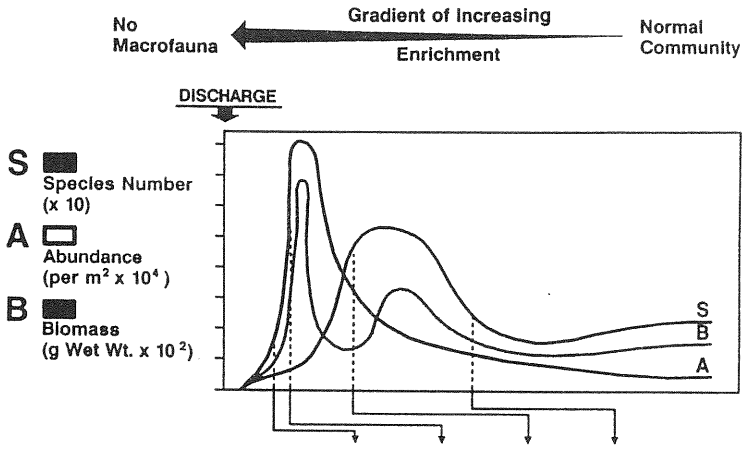
Bladder-wrack annual growth rate at different sampling stations has systematically been assessed since 1984 at Mönsterås recipient(Landner et al. 1994b). During the chlorate discharge period, up to 1987, the bladder-wrack was eliminated in a zone near the diffuser and further away the bladder-wrack growth was reduced (Lehtinen et al. 1988). After elimination of chlorate discharges in 1987, normal growth was re-established in the whole area, yet with abnormal densities (Notini 1991).

5.4.2 Effects on benthic fauna

Where impacts from pulping effluents occur at the community, the population, and even the within-organism levels, there are distinguishable gradients or zones of effects. Historically organic and nutrient enrichment were largely responsible for adverse environmental impacts from pulping discharges. There is also evidence for chemical toxicity at sites that are simultaneously experiencing enrichment effects. Where organic and nutrient enrichment are sufficiently controlled by process design and biological effluent treatment, community and population effects have not been observed.

However, these data are limited, and the possibility of chemical toxicity has not been fully explored (Owens 1991). Pulp and paper mills can discharge significant organic carbon and nutrient loads, which readily alter or degrade local habitats. A community and population gradient due to organic and nutrient enrichement has been proposed by Pearson & Rosenberg (1987)(Fig 24).

In Swedish studies, while no effect of pulp mill effluents on the colonization of sediment by settling organisms or on the burrowing activity of *Macoma baltica* was observed, disturbances, damages and diseases were noted locally on individual organisms and populations (Södergren 1993). The discharges altered the diversity and abundance of the benthic macrofauna close to the effluent source. The plant and animal species occuring along a gradient from the source to less polluted areas showed some common features, although there may be differences in species composition due to different phytobenthic substrata (Kautsky 1992). The most polluted parts of an area have abundant growth of few species. A transitory zone has a more even distribution of plant and animal species and functio-



		E 70	E 2	E 1	E 24	Station at Loch Eil
Principal Infaunal Taxa	Thyasira	-	-	17	933	
	Amphiura	3	7	187	267	
	Melinna	-	-	7	240	
	Glycera	3	7	7	50	
	Pholoe	30	267	83	67	
	Anaitides	127	157	-	-	
	Protodorvillea	3	1077	-	-	
	Tubificoides	810	1353	-	-	
	Capitella	27	77	-	-	
	Nereis	3	7	-	-	
Principal Epifaunal Taxa	Crangon allmani	x	xx	xxx	xxx	
	Crangon crangon	xx	xx	x	x	
	Hyas araneus	x	xx	x	x	
	Carcinus maenas	x	xx	x	x	
	Gadus morhua	x	x	x	x	

Figure 24. Model of biological responses of benthic fauna to organic enrichment by a pulp mill (Source: Pearson & Rosenberg 1987).

nal groups, while at the least-polluted areas number of different species increase. The findings by Kautsky (1992) can be concluded to be caused by eutrophication and enrichment, noting the similarity between his observations and the model gradient presented in figure 24.

Despite a major damage to the benthic communities that occured in 1980-1984 and was due to the chlorate discharge at that time, no direct detrimental effects on benthic flora and fauna could be related to the present BKME discharge from the mill (Landner et al. 1994b). Shell corrosion studies on the Baltic mussel, *Macoma baltica*, did not reflect any effluent-exposure-related increase in this type of damage. Recipient sampled shells compared with shells (*Macoma baltica*) from museum collections from the period of 1880–1930 were analyzed for frequency and severity of shell corrosion. It turned out that the historical material displayed a similar pattern of shell corrosion, although the average degree of corrosion was slighty lower (not statistically significant) than in the fresh material (Warén 1991).

Two meiofauna surveys in the recipient of the Iggesund pulp mill were performed in 1987 and 1991. During the intermediate period a new production line including modified cooking, oxygen delignification, low multiple chlorination and reinforced alkali extraction was installed. In 1987 the abundance of total meiofauna was lower at 3 stations, while the biomass was lower at all stations along a pollution gradient measured by sediment EOCl. Sensitive groups were ostracods, kinorhynchs, turbellarians and nematodes. In 1991, the area was still affected from the pulp mill and the abundance and biomass were lower at most stations. A comparison before and after the changes in the pulp producing processes including modified cooking, oxygen delignification and low multiple chlorination, showed that the abundance of ostracods had increased in 1991 and the trend for most meiofauna taxa is an increasing from 1987 to 1991 indicating a recovery (Sundelin & Eriksson 1994).

At Grand Praire (Canada) the responses of the river benthic populations showed only modest enrichment responses (Swanson et al.1993), with an increase in the numbers of organisms. However, pollution-sensitive organisms were still present in the river below both municipal sewage discharge and the mill discharge. There was no evidence that any species had suffered any effects from chemical toxicity. The benthic invertebrate community of the Wapiti River appeared to be healthy, and to have been so, in spite of twenty years of mill operation.

The effects on benthic fauna seem to be resticted to immediate discharge areas. The Environment/Cellulose II project (Södergren (1993) concluded that no biological effects on bottom-dwelling organisms are expected as a result of the long-range deposition of chlorinated organic material on remote area sea floor in the Baltic Sea. The levels of EOCl (as derived from the budget calculation) in surficial sediment of remote areas will remain below those where biological effects have been documented in laboratory experiments or observed in field studies in receiving waters. Although no effects are presumed to occur in the remote areas, the benthic organisms belonging to the lower trophic levels of the food web may serve as a transport medium transferring compounds accumulated from the sediment to higher trophic levels via the food web. These conclusions are, however, based on a limited set of biological observations and have to be reconsidered when new data emerge.

5.4.3 Effects on fish

The field studies made in the middle of the 1980s outside the Norrsundet mill at the coast of the Bothnian Bay resulted in a worldwide intrest focussing upon the chlorinated material as potentially responsible for the effects noted on within-organism, whole-organism and fish population levels (Södergren et al. 1988). Within-organism parameters include histopathology, liver size, hematology, serum chemistry and reproductive parameters such as gonad size. At the whole-organism level, commonly studied endpoints in the field include: condition factor, external gross pathology and parasite infection rates. Fish population endpoints have included the presence and distribution of fish species and the growth rates and mortality rates of particular species. The studies at the Norrsundet site were performed mainly during 1984 and 1985 (Hansson 1987, Andersson et al. 1988, Neuman & Karås 1988, Sandström et al. 1988, Sandström & Thoresson 1988, Lindesjöö & Thulin 1990). In some cases, effects observed in the receiving water outside a mill producing unbleached pulp and with good dilution conditions were compared to those from the main object of the investigation.

The investigation on whole-organism and within-organism levels revealed reduced gonad growth, enlarged liver, and strong induction of the EROD enzyme in the liver of feral perch, *Perca fluviatilis*, as far as 10 km from the discharge point. In addition, hematological and osmoregulatory responses were obtained. Reported disturbances were most pronounced 4.5 km from the outfall and moreover, the intensity decreased between 1984 and 1985. The results made the authors to believe that substances formed in the bleach plant, especially the chlorinated material, were responsible for induction of the effects noted in fish. The conclusion was based on the fact that the EOCl content in sediments, molluscs and fish was higher outside the Norrsundet mill and decreasing with the distance from the mill. Likewise, higher levels of PCDD/PCDFs were found in fish tissue, also decreasing with the distance. However, it was also noted that the levels of PCB and DDT decreased with the distance from the coast. The conclusion that the chlorinated material generated in the pulp mill bleach plant would have been exclusively responsible for the effects cannot be considered as justified for several reasons:

- The levels of non-chlorinated toxic substances were not measured at all, so their contribution to the toxicity was unknown.
- Non-chlorinated substances such as resin acids have long been known to contribute to within-organism level effects in fish.
- The mill was not operating normally during the most intensive period of investigations, which corresponded with the start-up period of a new process.

The latter resulted in frequent process disturbances which led to high discharges of COD and BOD as well as high black liquor carry-over from the digester to bleach plant. In these instances, the levels of all potential toxicants were higher than for a normally operating mill (Owens 1991). The COD load from the Norrsundet mill during 1983–1987 is presented in Figure 25.

The concomitantly performed fish population studies at the Norrsundet site showed significant changes in fish species number and distribution (Sandström et al. 1991). General patterns could be established, related to both organic enrichment and toxic pollution. Close to the mills, fish abundance was low with an absence of fish within 1–2 km of the mill discharge. At intermediary exposure, however, eutrophication caused very high fish biomasses and a community strongly dominated by cyprinids. The growth rates of perch and roach *Rutilus rutilus*, 2–4 km from the discharge, were significantly higher than in less exposed areas and the mortality rates were higher in exposed perch. High prevalances of fin erosion together with deformities of the gill cover on perch and deformities of the upper jaw of northern pike, *Esox lucius*, were found at Norrsundet in 1984.

Although all studied areas provided potentially good recruitment habitats, fry abundance was generally low. Studies on spawning on artificial substrates demonstrated that sufficent numbers of eggs were deposited even in the most effluent-exposed parts of the study area. No increased egg mortality could be noted , but at the stage close to hatching about 10% of the embryos were observed

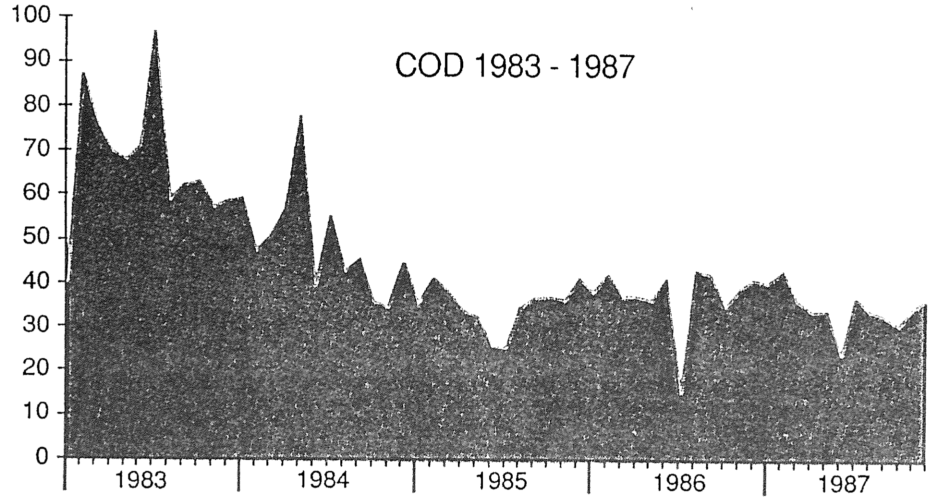


Figure 25. The COD load (t/d) from the Norrsundet mill in 1983-1987 (Source: Södergren 1988).

to be malformed, generally having sharp bends in the posterior part of the spinal cord. Exposed embryos were generally smaller than reference fishes, both when length and weight were compared. Larval sampling provided evidence for high mortality at or very close to hatching. Food and feeding conditions appeared to be of little importance for mortality. Two mortality causes were suggested: chronic failure of the parental reproductive system and/or acute toxicity to embryo or early larvae.

Based on the results presented by Sandström et al. (1991), Karås (1989) and Neuman and Karås (1988) it is clear that significant ecological effects were seen in the fish community. However, the effects on population structure and species diversity were of similar kind as those seen outside other mills without bleaching (Hansson 1987). The Norrsundet case study has been rewieved in detail by Owens (1991).

In field studies performed outside other Swedish pulp mills than Norrsundet, in both brackish and fresh water, varying responses in fish and fish populations have been noted (Tana et al. 1988, Grahn et al. 1991, Landner et al. 1994b). In these studies the exposure level from effluents was determined by the content of conjugated chlorophenolics and resin acids in the bile of fish (cf. Oikari and Ånäs 1985, Oikari and Holmbom 1986). In a brackish water area, several responses in the within-organism level were obtained, i.e. EROD-induction, changes of the white blood cell distribution, elevated liver ascorbic acid, liver cell structure and liver glycogen. The changes, for example, in enzyme activity did not correlate with levels of chlorinated phenols or resin acids in the bile of the fish studied. The highest EROD activity was found in fish from an area 10 km from the outfall of the two pulp mills in the Gävle Bight (Lehtinen et al. 1989). On the population level, cyprinid fish dominated close to the discharges, though without a total absence of fish at 0–2 km from the outlet as observed in Norrsundet (cf. Sandström et al. 1988).

At the Mönsterås site, studies of the composition, abundance and biomass of the fish community revealed that even in the most BKME-exposed area only minor effects were detected. Ruffe, *Gymnocephalus cernua*, populations increased slightly with no changes in perch or other species (Landner et al. 1994b). With regard to stationary species such as perch, pike, minnow, and stickleback, there was no tendency to reduced abundance of fry at the presumably most wastewater-exposed area. The physiological status of perch, studied by a set of physiological and biochemical measurements widely refered as biomarkers, revealed that even in the most BKME-exposed area, only minor effects were detected (Landner et al. 1994b). These effects were related to eutrophication/enrichment rather than to the action of toxic substances.

The effects seen in a fresh water receiving area at Skoghall, Sweden, with poor dilution capacity (about 100 times) were surprisingly small (Grahn et al. 1991). The level of conjugated chlorophenols was intermediary high closest to the discharge point and lower in the more distant area. The only obvious and well documented effect found at the Skoghall site was the high density of cyprinid fish due to eutrophication. No changes in the activity in EROD could be detected between exposure and reference areas.

All in all, the results from field studies including within-organism, whole-organism and fish population studies performed in other Swedish recipients than Norrsundet show a variety of responses, which do not correlate with the exposure situation as illustrated by analysis of chlorophenols and resin acids in fish bile. The follow-up studies at Norrsundet in 1988–1990 have shown improved benthic conditions, no further incidents of fin erosion or malformations, decreased effects in fish population effects, normalized perch gonad size and improvement in various biomarker responses (Grahn et al. 1992, Förlin et al. 1991). These improvements are a result of considerable decrease in effluent loading and proper operation of the mill (Landner 1990). The COD, for example, decreased from 80 t/day in 1984 to 38 t/day in 1991. At the same time the AOX load decreased by more than a half being 1.2 kg/t in 1991.

Recent field investigations in North America regarding physiological status and reproductory effects in different fish species downstream pulp mills have revealed some of the same effects as those seen in the Norrsundet study (Munkittrick et al. 1991). A study was performed downstream (Jackfish Bay) a pulp mill with conventional bleaching technology and without external treatment. The results showed changes in LSI-values(liver somatic index), elevated mixed-function oxygenase activities, lower gonad-somatic indices and an increased age to maturity in white sucker, *Catostomus commersoni*. The fish had also significant reduction in plasma steroid levels throughout the year. Introduction of secondary treatment did not eliminate enzyme induction or impact on steroid levels in fish. Interestingly, a shutdown of the mill for two weeks eliminated EROD induction but did not eliminate the steroid effect. The short duration of MFO-induction after shutdown suggests that induction is not related to contamination by TCDD-like compounds. Moreover, impacts are not related to food chain contamination, and plasma steroid reduction and MFO induction are not causally related.

The study was repeated below other Canadian mills to evaluate whether the discharge of effluent from other pulp mills than Jackfish Bay was associated with physiological and biochemical disruptions in feral fish, whether there was any correlation between waste treatment and the presence of biological responses in wild fish, and whether there was any association between the use of chlorine as a bleaching agent and these responses (Munkittrick et al. 1994) . Although white suckers collected near bleached kraft mills exhibited the highest EROD induction and dioxin levels, elevated enzyme activity was observed in fish from sites that did not use chlorine bleaching , and depressions in plasma sex steroids levels were not correlated with the level of EROD activity. The absence of chlorine bleaching or the presence of secondary treatment did not eliminate responses in fish, including decreased circulating levels of sex steroids, decreased gonadal size and increased liver size. The survey showed that

(a) induction of hepatic EROD enzymes and depressions of plasma sex steroid levels during gonadal growth are found downstream of several pulp mills;
(b) these changes are seen at some mills without chlorine bleaching and at mills that have secondary treatment;
(c) substantial dilutions of non-toxic effluent do not appear to remove these responses;
(d) the dominant factor determining the presence or absence of responses appeared to be dilution; and
(e) lab-toxicity tests on invertebrates and fish could not predict the presence of the responses in wild fish.

In a northern Alberta riverine ecosystem the potential impact of bleached kraft mill effluent discharges on fish population and fish health was studied (Swanson et al. 1993). The study was made to add to the knowledge on pulp mill effluent impacts in receiving waters caused by modern mills with secondary treatment and upgraded processes such as chlorine dioxide substitution or oxygen delignification. At the time of sampling, the mill had chlorine substitution raised from 25% to 70%, oxygen reinforcement of the first extraction stage was started and the hypochlorite stage was eliminated. The mill had secondary treatment in an aerated lagoon. The study produced the following conclusions:

An understanding of natural habitats and seasonal fish movement was vital for interpretation of exposure to mill effluent and possible relations between exposure and effects. Natural habitat gradients occurred from upstream to downstream in the river system. The quality of fish habitat changed along these gradients influencing when and where fish were found. Once the interaction of habitat and fish distribution was understood, the degree of exposure to mill effluent to be expected for the two main study species, longnose sucker, *Catostomus catostomus* and mountain whitefish, *Prosopium williamsoni*, was also understood.

Growth rates at the polluted areas were similar to unpolluted reference sites. Mountain whitefish and longnose sucker were growing and reproducing succesfully. The age structure of the populations showed that there have been no losses of age classes through reproductive or recruitment failures.

The main effects on fish population parameters observed in the study were caused by natural phenomena. The river flood greatly altered or eliminated habitats and totally changed fish distribution for several months. Recruitment of young-of-the-year was also disrupted. Other important phenomena affecting species distribution, condition factors and relative abundance were habitat quality, food supply, and seasonal and daily fluctuations of the flood.

There was no evidence of correlations between indicators of exposure (body burdens of contaminants, liver size or liver detocification enzymes) and population-level effects. The data indicated gradients of responses to habitats (especially of responses for parameters such as condition factor and gonad size).

Since the early 1960s, numerous studies and surveys have been made on species composition and relative abundance of fish using survey fishings in recipient areas of the Finnish wood processing industry. Unfortunately only a small portion of the existing information has been published (Hakkari 1992). Most of the studies have been made for regulatory purposes lacking mill data and information of different effluent parameters. Effects described from Swedish recipients have also been observed in a Finnish lake ecosystems receiving pulp or paper mill effluents (Hakkari 1992). Hakkari concluded the effluents from pulp and paper mills to cause the following zoning of the lake ecosystem:

1) Zone of inhibition
Because of lack of oxygen, toxic compounds and suspended solids, the area nearest the mill usually has no or only one permanent stock during some seasons. In most cases, this zone has become smaller or has disappeared altogether from Finnish waters during the last 10 years as a result of improved pulping technology and secondary treatment.

2) Zone of strong eutrophication and sublethal toxicity
The concentration of nutrients is lower than in the first zone, but maximum biological production is found in this zone because of decreasing toxic effects and a moderate oxygen saturation. Cyprinids are dominating.

3) Zone of slight eutrophication
The concentration of nutrients has decreased, but is still above natural levels. Some decrease in the oxygen exists in the hypolimnion.
The number of different fish species increase.

4) Zone of natural water quality
The concentration of total phosphorus is low. Usually there is no remarkable decrease in oxygen in the hypolimnion during stagnation and species diversity is natural.

Most of the studies made in Finnish mills present data from separate experiments on within-organism, whole-organism levels without simultaneous assessment on population or community levels.

5.4.4 Effects on fish, within-organism level

Within-organism parameters include for example histopathology, liver size and metabolism, hematology and serum chemistry and reproductive parameters such as gonad size. Physiological and biochemical measurements have been widely referred to as *biomarkers*, and their application to organisms exposed to pulping effluents have been reviewed by McLeay (1987), Kovacs (1986) and Owens (1991). Initially, clinical measurements from mammalian research were utilized, such as during the exposure of salmonids to primary treated BKME (McLeay and Brown 1975, Soivio et al. 1979). Physiological and biochemical responses to pulping discharges have been investigated primarly in Scandinavia and Canada.

In contaminated habitats organisms may demonstrate pathological effects in either gross morphology or histology. Vertebral and spinal deformities in the Baltic Sea fourhorn sculpin have been intensively studied. Like many fish abnormalities in natural settings, these deformities are common with background rates of about 20%. Near Baltic Sea bleached kraft mills the rates of these deformities ranged from 60% near the Husum mill to near background at the Norrsundet (16%) and the Wisaforest mill (9%). Water colum, sediment, or body burden analyses were not available from field studies and deformity rates at control sites increased with water depth and low temperature (Bengtsson 1987).

Fin erosion in perch and ruffe and bone deformities in pike observed outside Norrsundet in 1984-85 (Lindesjöö & Thulin 1990, 1992) have not been found at other sites receiving both treated and untreated effluents (Landner et al. 1994, Swanson et al. 1993, McMaster et al. 1991). Only a few studies have been carried out on histology and histopathology in field experiments. Treated paper mill effluents have been observed to cause marked depletion of liver glycogen, necrosis of single hepatocytes and a higher degree of liver parasitization (Bucher et al. 1992). Recent laboratory experiments with untreated TMP-effluent have indicated the same kind of effects in liver structure, with a clear increase of necrotic hepatocytes (Johnsen et al. 1993).

There is a real need to establish indicators of physiological fitness which would not fluctuate on a seasonal basis. Studies at Jackfish Bay have demonstrated numerous changes related to exposure, including effects on red blood cells, white blood cells, conjugation enzymes and changes in plasma levels of a number of parameters, including glucose, protein and lactate (McMaster 1991, Munkittrick et al. 1994, Smith et al. 1991). Other studies of pulp mill effects on fish populations have also demonstrated changes in a number of nonspecific parameters (Tana and Nikunen 1986, Andersson et al. 1988, Hodson et al. 1992, Servos et al. 1992, Oikari et al. 1985b). However, these changes have not been directly linked with changes in whole organism performance and are often quite variable. Although several studies, using a number of biochemical parameters, have indicated statistically significant differences between sites, few generalized responses have been found. Hematocrit levels in white sucker collected near North American pulp mills was found to decrease (McMaster 1991), increase (Hodson et al. 1992) or not to change (Servos et al. 1992).

Several other examples can be given for other parameters in fish from other receiving waters. Although inter-site comparisons are difficult because of differences in mill production, bleaching and treatment characteristics, and differences in the receiving environments, the minimum and maximum hematocrits observed in the above studies were recorded at reference sites suggesting that all exposed sites were within the normal range of variability for this species. Physiological parameters have been observed to show a log-normal distribution in perch and a natural variation between 10–40% (Monfelt et al. 1991) Owens (1991) reviewed more than 20 biochemical measurements conducted on perch by Swedish scientists (reviewed in Södergren 1989) and concluded that (a) the biochemical changes could not be linked to the observed population impacts and (b) the primary difficulties associated with clinical measurements currently used are their variability and lack of specificity.

The most frequent responses at reproductive measuremets has been a decrease in gonad size relative to somatic weight (GSI). Gonad size is generally related to reproductive capacity, but the gonad size fluctuates during the annual sexual cycle and the reproductive status must be precisely known to interpret these data. In addition to GSI, other reproductive data have been gathered at several BKME sites. A set of related measurements is preferable when defining critical endpoints such as reproduction. Varying changes have been observed on larval abundance, sexual maturity and secondary sexual characteristics (Sandström et al. 1988, Munkkittrick et al. 1991, Swanson et al. 1993). More sophisticated analyses include circulating levels of sex steroids and the pituitary hormones which directly control steroid production. The lower levels of circulating gonadal sex steroids in white sucker from Jackfish Bay are related to an inability to properly regulate the production of these steroids (Van Der Kraak et al. 1992) and have been directly linked with changes in reproductive performance (McMaster et al. 1991).

At La Tuque mill, Canada, no significant effects were observed at the discharge in neither males nor females, although testosterone levels were lower 100 km downstream (Hodson et al. 1992). The measurements of sex steroid levels has some disadvantages, as steroid titers fluctuate within reproductive development and are often undetectable during annual periods of gonadal regression. Levels of reproductive sex steroids in some species are also sensitive to handling and holding stress during sampling (Sumpter et al. 1987, Van der Kraak et al. 1992) which could possibly affect interpretation of the data.

One of the most widely used biomarkers related to pulp and paper mill effluents has been the induction of MFO or cytochrome P450. Cytochrome P450 is a common name for a family of isoenzymes which are found in cells throughout different organism levels, from prokaryotes (unicellular) to eukaryotes (multicellular). These enzymes transform several endogenous and exogenous organic susbtances to more hydrophilic compounds which are more readily excreted. Many environmental substances (e.g. aromatic or halogenated hydrocarbons) are known to increase the amount of cytochrome P450IA. This induction can be detected by measuring the activity of the enzyme EROD (7-ethoxyresorufin 0-deethylase) (Lindström-Seppä et al. 1992b).

EROD or P4501A induction has been observed at numerous BKME sites in both feral (Andersson et al. 1988, Lindström-Seppä 1990, Munkkittrick et al. 1991, Kloepper-Sams 1992, Landner et al. 1994b) and caged fish (Lindström-Seppä and Oikari 1989b). The degree of induction may vary between species (Lindström-Seppä 1990), and females of some species have reduced induction prior to and during spawning. Induction values have ranged from none (Landner et al. 1994b) to up to 30 fold (Kloepper-Sams 1992).

EROD induction has also been observed in feral and caged fish in the recipient of an unbleached sulfite mill (Lindström-Seppä et al. 1992a) and at a mechanical pulp mill site (Munkittrick et al. 1994). A rapid decrease of EROD induction to reference values has been observed during a mill shutdown at Jackfish Bay implicating soluble, rapidly metabolized substances being responsible for induction.

At the first Conference on Environmental Impacts of Pulp Mill Effluents (Saltsjöbaden, Stockholm) measurements of MFO induction in fish exposed to BKME were confirmed and extended to mills not using chlorine bleaching. MFO activity was associated in field studies with effects on fish, particularly regulation of steroid hormones. Unknowns arising from the 1992 meeting included (Hodson 1994):

- mechanisms linking MFO induction to other toxic effects
- sources of inducers
- effects of effluent treatment
- role of chlorine bleaching
- the nature and identity of inducers.
- the environmental fate and distribution of inducers in the environment.

At the second Conference on Environmental Fate and Effects of Bleached Pulp Mill Effluents Hodson (1994) reviewed advances since 1992. While known inducers like TCDD/TCDF are quite toxic and may have reproductive effects, the link to steroid effects in effluent exposed fish is not clear; there appear to be multiple effects on the steroid regulatory system. Induction can be caused by effluents or extracts from pulp mills using either chlorine bleaching or non-chlorine bleaching, and one of the most potent sources within mills is spent cooking liquor. Additional contributions from C and E-stage effluents implies further release of inducers from lignin, or increased potency of inducers due to chlorination. However, optimized waste treatment processes reduce induction potency of effluents. Induction downstream of pulp mill can be found at distances up to 90–100 km, implying environmental persistence of inducers, but they are readily metabolized and excreted by fish. The available evidence also shows that EROD induction is related to exposure to pulp mill effluents, but not necesarily to adverse effects.

Table 19. Whole- and within-organism responses in various feral fish species caughtfrom different pulp mill receiving waters. (Sources: Förlin et al. 1991. Landner et al. 1994b, Kloepper-Sams 1992, Kantoniemi 1994).

Variable	A	B	C	D	E
Condition factor	nd	0	0	+	nd
LSI	++(0)	0	0	+	nd
GSI	+++(+)	0	0	nd	nd
EROD	+++(+)	0	+++	+	+
UDP-GT	nd	nd	nd	+	0
Liver glycogen	+(+)	0	nd	nd	nd
Plasma lactate	+++(0)	nd	0	nd	nd
Plasma chloride	++(+)	nd	nd	0	0
Hematocrit	++(+)	0	0	nd	nd
WBC numbers	++(nd)	0	0	nd	nd
ALA-D	+++(nd)	nd	nd	nd	nd
Histopathology	nd(nd)	nd	0	nd	nd
Immarure RBC	nd(nd)	+	nd	nd	nd

+ = response compared to control, strenght increasing with number of +
0 = no response compared to control
nd = not detected
A=Norrsundet 1984()=Norrsundet 1990;
B=Mönsterås 1991,low Cl+ext.treat.
C=Grand Prairie 1991,D70+ext.treat.
D=Savon Sellu 1991, unbleached
E=Kaukas 1994,D100+ext.treat.

Field studies show a vide variation in the extent and the degree of whole- and within-organism responses at BKMe sites. The tecnological development in bleaching and treatment processes has led to a decrease in responses in the receiving waters (Table 19).

An example is from Lake Saimaa in the south eastern part of Finland (Oikari and Holmbom 1994). An integreated mill producing kraft pulp and printing paper from hardwood and softwood changed the bleaching to complete substitution to chlorine dioxide and replaced the aerated lagoons by an activated sludge plant in the treatment of effluents. These process and treatment alterations led to dramatic reductions in organochlorines, such as chlorinated phenolics, both in lake and fish. The induction of EROD activities in fish caged in the receiving water were also markedly reduced (Figure 26). Based on the responses in fish, the novel environmental technology in the mill was reflected as less exposure and effects in the aquatic biota (Oikari and Holmbom 1994).

Another expample is the reneval of an old fashioned mill with two production lines in eastern Finland. The mill tripled its production and changed the bleaching to 100% chlorine dioxide on one line and peroxide on the other line. The effluents are treated in an activated sludge plant and tertiary stabilization pond before being released to the river recipient. Biomarker studies before and after the start of the new mill show no adverse changes in fish due to the increase of production (Tana & Lehtinen 1995). In this study a decrease in the activity of EROD was observed in fish caged further away from the mill outlet though the undiluted mill effluent caused a 3-4 fold increase in the enzyme activity in fish caged in the tertiary treatment stabilization pond. The same result was observed in a caging

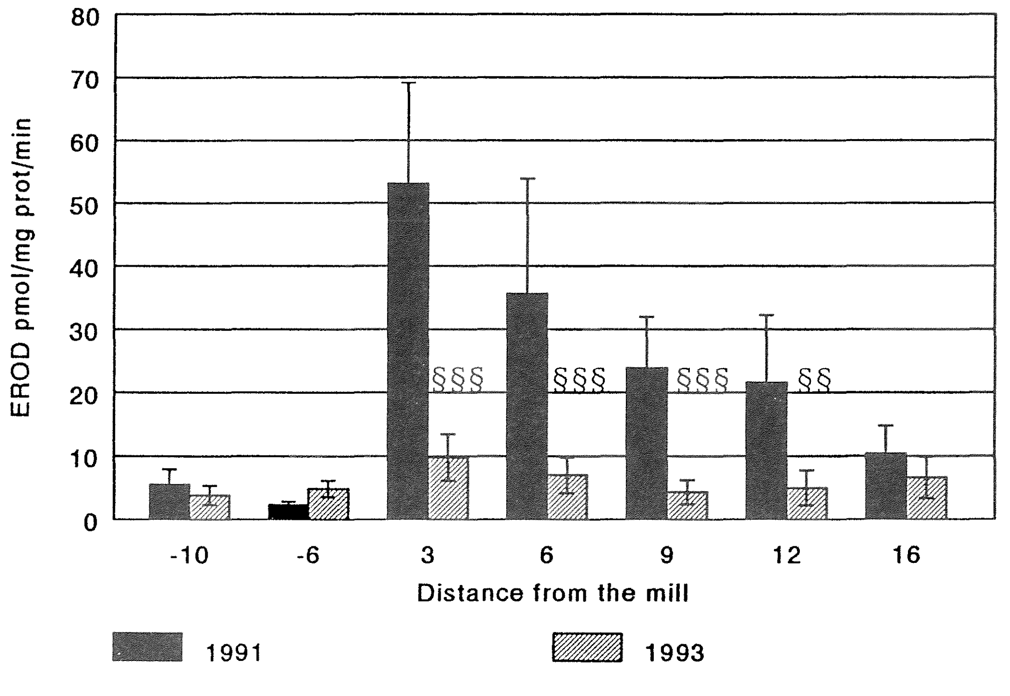


Figure 26. Changes in EROD activity in white fish caged in a mill recipient before and after modifications in bleaching and secondary treatment. Statistical significance between years: § = P<0.05; §§ = P<0.01; §§§ = P<0.001 (Source: Petänen et al. 1993)

study with mussels (Mäkelä et al. 1992). The receiving water is very humic and the dissolved organic matter (DOM) increases at the more distant areas from the mill. As total DOM as such is an important factor controlling the bioavailability of xenobiotics in natural waters (Kukkonen 1991) the effects of humic waters on fish physiology cannot be discerned from mill effluent effects. For the time being no field studies are available on TCF processes.

From the recent field studies of the environmental impact of BKMEs (Swanson et al. 1993, Williams et al. 1991, Grahn et al. 1991, Landner et al. 1994b, Munkittrick et al. 1994) it is not possible to infer any general effect model. The "typical" effect pattern, observed earlier in fish from receiving waters outside bleached kraft pulp mills, using an older generation technology (Södergren 1989), even with secondary effluent treatment (Munkittrick 1991), has not been confirmed. The available field data from mills which are propely sited, under operational control and have efficient biological treatment of the effluents show that fish and benthic populations appear to be healthy (Owens & Lehtinen 1995, in press). Studies of the environmental impact of BKMEs must be carried out as integrated investigations including both physiological and ecological aspects and be based on thorough knowledge about the production processes and the emitted substances or groups of substances. With the conversion of mills to ECF and TCF processes, researchers must better define exposure, mill conditions, the site habitat and hydrology, and historical impacts on the receiving waters before drawing unwarranted conclusions. Furthermore, the ecological relevance of the various biomarkers, or combination of biomarkers, used in the field studies must be evaluated (cf. Owens 1991), before they are recommended for routine monitoring programs.

Summary

6

6.1 Background

The issue of the possible environmental impact of chlorinated organic compounds being formed during the bleaching of pulp with chlorine and/or hypochlorite was first raised back in the 1970s. However, it was first in the beginning of the 1980s that more systematic studies were undertaken of the nature, the properties, the amount and effects of this chlorinated organic material. Such studies were mainly initiated by the pulp industry and conducted by research institutes in cooperation with the industry.

By the middle of the 1980s, a series of field studies in the receiving waters of a bleached kraft pulp mill in Sweden was initiated by the Swedish EPA. When the results from these studies were presented, usually without any attempt to relate observed biological effects with process parameters in the mill or with the actual exposure to specific chlorinated organic compounds, a major controversy came up regarding the environmental significance of pulp mill related chlorinated organics (cf. Folke 1989; Folke et al. 1991; O'Connor et al. 1993).

In the public debate that followed, and which strongly influenced also the regulatory agencies in Europe and North America, a great deal of confusion was seen. An often used argument was that since some of the most harmful compounds in the environment, such as DDT and PCB, are chlorinated organics, and are persistent, bioaccumulative and highly toxic, it is probable that the chlorinated organics with pulp mill origin are equally harmful to the environment. Therefore, the discharge of such compounds should not be allowed, and chlorine must be phased out as a bleaching chemical. In fact, both the environmental NGOs and the regulatory agencies failed to account for the great variability in chemical and toxicological properties of different classes of chlorinated organics. The also refused to consider the upcoming knowledge about the abundance of naturally occuring chlorinated organic compounds in the environment (cf. Grimvall 1993) in their crusade against the use of chlorine as a bleaching chemical. Even worse, they showed very limited interest to establish a clear scientific relationship between the pulp mill generated chlorinated organics and the observed biological effects in the pulp mill receiving waters.

Thus, the dramatic transformation of the pulp bleaching technology in mills throughout the world that was implemented during the last 10 years, and which resulted in almost total phase-out of chlorine, was not supported by firm scientific evidence about causal relationship between pulp mill-generated chlorinated organics and the biological or ecological effects. In stead, the transformation process was driven by suspicions and weak, circumstancial evidence that the actual chlorinated organics might be harmful to ecosystems (Reeve 1993; Clark 1994).

6.2 Technical development

As a result of the above summarized debate, the pulp and paper mill industry in most industrialiazed countries has been forced, by consumer pressure groups and regulatory authorities, into huge investments in technologies which have contributed to significantly reduce the AOX discharges from the mills. As a first step, the kraft industry went for low chlorine multiple bleaching and an increased substitution of chlorine gas with chlorine dioxide in the first stage of the bleaching sequence. These process modifications as a whole were environmentally beneficial, because of the strong reduction in formation of polychlorinated dioxins and furans (Kringstad et al. 1989; Folke et al. 1991; Folke & Renberg 1994). Subsequently, introduction of oxygen delignification, modified or extended cooking together with effective biological effluent treatment, as well as total elimination of chlorine in the bleaching sequence (ECF bleaching) occured (Fig 27). Today, several major mills in the world have replaced chlorine dioxide with hydrogen peroxide, ozone or peroxy acids (TCF blaching), at least for production of certain qualities of bleached pulp.

Fortunately, these investments were generally accompanied by improved operation practices, upgraded brown stock washing systems which reduced the carry-over of black liquore to the bleach plant, more careful dosage of bleach chemicals, and installation of spill recovery systems, which reduced the discharges of unchlorinated organics from mills. Scientific evidence suggests that the reduction in total amount of organics discharged, which usually accompanied the implementation of AOX control measures, was the real cause for the reduction of the toxicity and the environmental impact of the effluents.

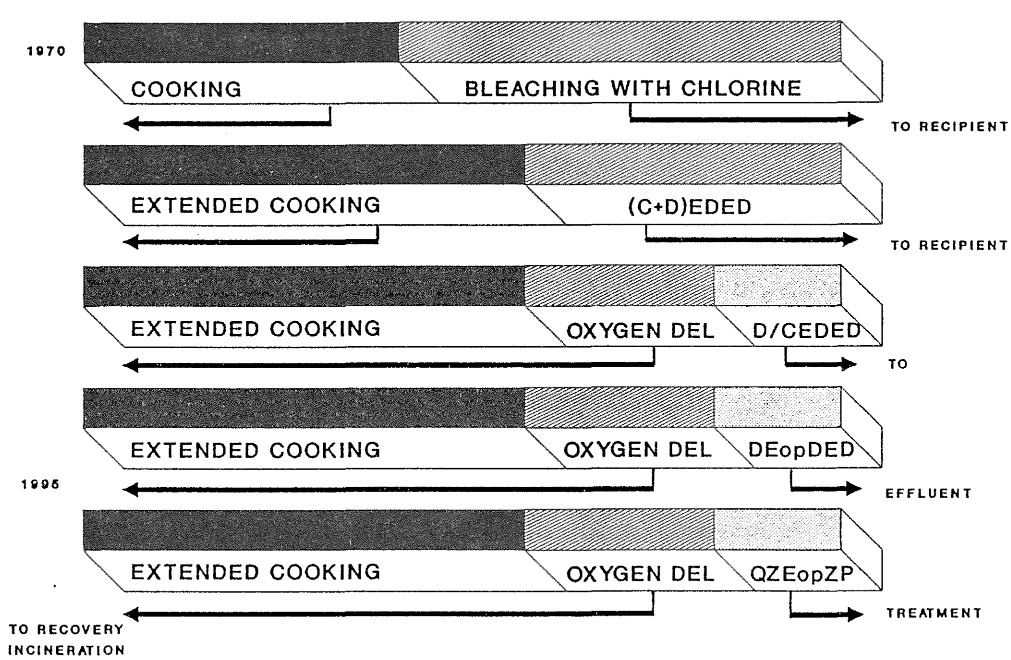


Figure 27. Developments in pulping, bleaching and discharges. (Sources: Annergren 1993; Kymmene 1994).

6.3 Exposure analysis

In the assessment of of the environmental impact of pulp mill effluents, the first phase normally includes an exposure analysis. This means that the concentrations of various compounds or groups of compounds, occuring in the effluents, to which the aquatic ecosystem may be exposed, are estimated. Based on the consideration that compounds being persistent to biochemical degradation may give rise to long-term and wide-spread exposure, it is pertinent to focus on this fraction in the effluents. The fraction of organic compounds in the effluents which is not readily degradable can be characterized by the difference COD–BOD_7. However, this analysis does not provide any information as to the harmfulness of this fraction. Figure 28 shows, in a conceptual way, the relation between BOD, COD and DOC (dissolved organic carbon). In many mills, with well ventilated recipients, where the effluents are rapidly diluted, it might be more important to reduce the discharges of the fraction COD–BOD_7 than reducing BOD. The choice of bleach chemicals in the final bleaching does not affect the amount of COD–BOD_7 very much, but the process design prior to final bleaching does, i.e. extended cooking, improved washing, oxygen delignification, etc.

In a modern kraft mill, designed for ECF or TCF bleaching, the discharge of polychlorinated phenolics, dioxins or furans is not an issue of concern. Instead, non-chlorinated compounds such as resin acids and fatty acids, plant sterols and other wood extractives, as well as chelating agents are currently attracting the main interest.

The actual discharges of wood extractives largely depend on the size of the wash losses and on operational standard of the mill, as well as on the type and

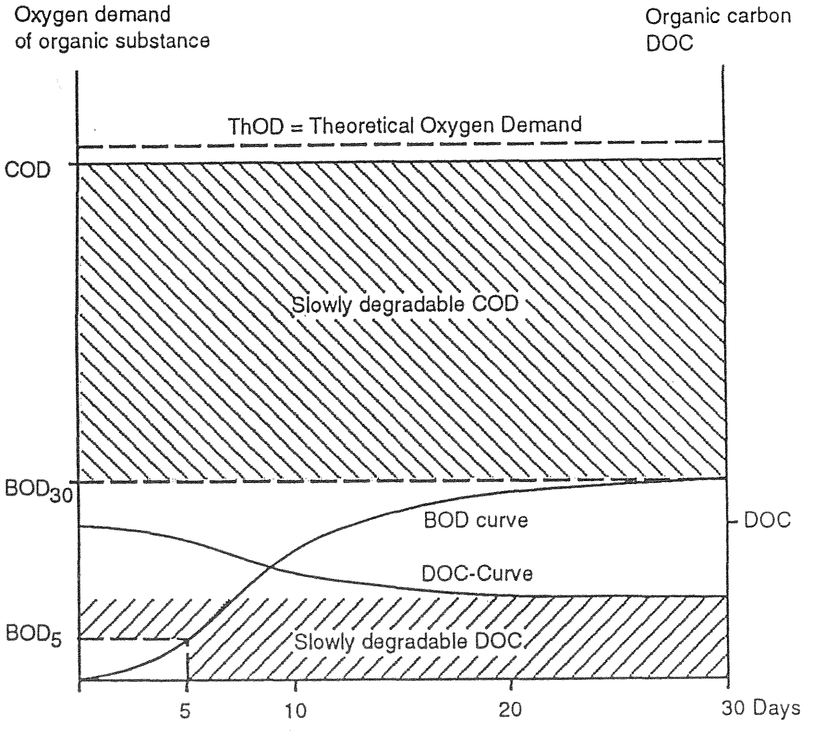


Figure 28. Conceptual illustration of the relation COD, DOC and BOB. (Source: Folke et al. 1993a).

extent of effluent treatment. Chelating agents, such as EDTA and DTPA, are used in connection with TCF bleaching. These compounds usually resist biological effluent treatment and may, in certain cases, contribute to eutrophication of receiving waters, due to their content of nitrogen and their tendency to stimulate phosphorus uptake in algae (Walterson & Landner 1994).

Many older field studies aiming at the assessment of environmental impacts of pulp mill effluents did not include any specific (or unspecific) biomarkers for recent exposure. This was particularly true for the original ""Norrsundet studies" conducted within the Environment-Cellulose project (Andersson et al. 1988; Södergren 1988). However, most other Scandinavian field workers (Oikari & Holmbom 1986; 1994; Oikari et al. 1985b; Grahn et al. 1991; Landner et al. 1994b; Tana & Lehtinen 1995) have tried to assess the actual exposure to pulp mill compounds of those fish populations that were simultaneously investigated with respect to physiological and other disturbances, by means of analysis of fish bile for conjugates of chlorinated phenolics and resin acids and fatty acids.

Another measurement, that was originally thought to be a convenient biomarker for effect in fish but in fact turned out to be relatively good biomarker of *exposure* (although unspecific) to pulp mill compounds, is the level of induction of the MFO-enzyme EROD. Recent studies have demonstrated that a majority of tested pulp mill effluents contain substances having the capacity to induce this enzyme. It should be pointed out, however, that the enzyme is induced not only by chlorinated organic compounds, but also by various unchlorinated substances.

6.4 Effect analysis

In this phase of assessment of the potential environmental hazards of pulp mill effluents, the potency of individual compounds to produce toxic responses in various aquatic species, communities and ecosystems is analyzed. The potency of whole mill effluents or fractions of such effluents to produce biological effects is also assessed, and dose-response relationships should, in principle, be established. This requires a good description of the exposure conditions, and in order to assist the industry in their process development, the analysis should preferably result in an identification of the compounds or process steps that are responsible for inducing the effects observed.

Unfortunately, this latter goal has practically never been fulfilled in the stidies reviewed in this report. Especially the older literature does not provide information useful to identify the real causes of various effects, including acute lethal effects. The great majority of older studies have been performed with untreated or treated whole mill effluents, and in most cases, information on process parameters, bleaching sequence, water consumption, etc. was lacking. In some cases, specific compounds such as chlorinated phenolics or resin acids have been tested, but only seldom these tests have been conducted at realistic environmental concentrations or under long-term exposure.

Already in the middle of the 1970s, Canadian researchers showed that another category of wood extractives than the resin and fatty acids, namely sterols, are acutely toxic to fish (Leach et al. 1975). More recently it has been shown that wood-related sterols interfere with hormonal status in fish. Furthermore, masculinization of female fish occured in receiving waters of pulp mill effluents (Bortone et al. 1989), as well as when fish was exposed to pulp mill effluents in the laboratory (Drysdale & Bartone 1989). Low levels of beta-sitosterol and related compounds caused stimulated growth and responses in metabolic variables in rainbow trout (Lehtinen et al. 1993), and reduced reproductive fitness in other species of fish (MacClatchy & Van Der Kraak 1994). Both microbiologically metabolized and unmetabolized wood sterols were shown to interfere with hormonal regulation in fish (Denton et al. 1985).

In summary, it seems that among the various compounds in pulp mill effluents, the group wood extractives may be regarded as one of the most important among the effect-causing agents, which may interfere with aquatic organisms at various levels. It may also be possible that several of the effects of pulp mill effluents reported in the past, and which routinely assigned to chlorinated organics, in fact were caused by one or several compounds among the wood extractives, which have no direct relationship to pulp bleaching. The pulp and paper industry is not necessarily unique when it comes to discharges of plant related compounds which mimic hormones in fish. In this connection, urban sewage and agricultural land runoff may be significant contributors to this category of ecosystem disturbing substances.

An overall evaluation and synthesis of the great amount of recent laboratory and model ecosystem tests as well as field studies with whole mill effluents from bleached kraft mills allow us to draw the following conclusions:

- Toxic responses caused by whole mill effluents from mills using the process technology typical for the period up to 1988 and with AOX releases above 1.5 kg/ton pulp, are generally higher than the responses caused by effluents from modern mills with AOX levels below 1.5 kg/ton pulp. This seems to be largely related to the operational standard of the mill.
- Toxic responses caused by whole mill effluents from modern mills (AOX below 1.5 kg/ton pulp) are generally very low, and show no variation related to the actual AOX release. This indicates that, at least in this category of mills, the chlorinated organics in the effluents do not contribute significantly to the toxicity of the effluents.
- A comparison of toxic responses of bleach plant and whole mill effluents from mills using different schemes for non-chlorine bleaching, i.e. ECF versus TCF bleaching, shows that neither technical concept invariably produces effluents with a lower toxic potency. Thus, according to studies made to date, ECF and TCF bleaching are not possible to separate in terms of their potential to produce detrimental effects in the aquatic ecosystem.
- Relative merits of ECF versus TCF are not consistent due to different experimental strategies in test procedures and also to non-bleaching factors within the different mills.
- Secondary treatment of effluents usually tends to decrease the toxicity of the effluents and according to model ecosystem studies both functional and structural effects on ecosystem level are alleviated after external treatment.
- Recent model ecosystem studies have indicated a correlation between effluent COD and the effects observed. These findings which, however, need further complementary recearch suggest that it is not a question of whether to use ECF or TCF as the choice of bleaching, but rather to improve the pulping operation in itself.
- Field studies show a wide variation in the extent and degree of whole- and within organism responses at BKME sites. From recent field studies of the environmental impact of BKMEs outside modern mills it is not possible to infer any general effect model. The available data from mills which are pro pely sited, under operational control and have efficient biological treatment show that fish and benthic populations appear to be healthy. In this respect each mill site is unique.
- Interpretation of biomarker responses is diffuse and the relation between biomarker responses and population and community level effects are still

unknown. Biomarkers related to reproduction and energy metabolism should be emphasized in future studies.
Furthermore, the ecological relevance of various biomarkers, or combination of biomarkers, used in the field studies must be evaluated before they are further used and recommended for routine monitoring programs.

- It seems that environmental impacts of modern mills cannot be predicted by knowing the bleaching sequences and the future environmental impact evaluations should concentrate more on other pre-bleaching processes.

Bleaching effluents

Selenastrum: ODEoD>OZP,OPZ

Ceriodaphnia,
Fatheaded Minnow
Trout MFO: OQP,OZEP>ODE

Zebra fish:
Sub-acute Tests: ECF = TCF

Combined Mill Effluents

Acute tests
Microtox
Ceriodaphnia: ECF = TCF

Sub-acute Tests
Zebra fish: ECF > TCF

Ceriodaphnia
Algae: ECF = TCF

Conclusions from the 2nd International Conference on Environmental Fate and Effects of Bleached Pulp Mill Effluents

* Biotreatment significantly reduced biological effects

* Pulping Effluent > Bleaching Effluent

* ECF = TCF
* ECF < TCF
* ECF > TCF

Figure 29. A comparison of the toxic responses of bleach plant and whole mill effluents from production of ECF or TCF pulp and conclusions from poster presentations at the 2nd International Conference on Environmental Fate and Effects of Bleached Pulp Mill Effluents, November 1994 Vancouver. (Source: Kovacs et al. 1995)

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Documentation page

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Author(s)	Jukka Tana and Karl-Johan Lehtinen (Finnish Environmental Research Group)	
Title of publication	The aquatic environmental impact of pulping and bleaching operations – an overview	
Parts of publication/ other project publications	This project has produced five other publications before this report.	
Abstract	The environmental impact of pulping and bleaching operations along with the technical development of bleaching procedures are discussed in the present report. Scientific evidence suggest that the reduction of the total amount of organics discharged, which usually accompanied the implementation of AOX control measures, was the real cause for reduction of toxicity and environmental impact of effluents. Toxic responses from modern mills are generally very low and show no variation related to the AOX release. According to studies made to date neither ECF nor TCF bleaching concepts invariably produces effluents with a lower toxic potency than the other. External treatment decreases the toxicity of effluents. From recent field studies of the environmental impact of BKMEs outside modern mills it is not possible to infer any general effect model. It seems that environmental impacts of modern mills cannot be predicted by knowing the bleaching sequences and the future environmental impact evaluations should concentrate more on other processes related to pre-bleaching.	
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Tekijä(t)	Jukka Tana ja Karl-Johan Lehtinen (Suomen Ympäristötutkijaryhmä Oy)	
Julkaisun nimi	Valkaistun massan tuotannosta aiheutuvien jätevesien ympäristövaikutusten arviointi – yleiskatsaus	
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Projektista on ilmestynyt viisi julkaisua aikaisemmin.	
Tiivistelmä	Tämän kirjallisuusselvityksen tavoitteena on ollut laatia viimeisimpään tutkimustietoon perustuva katsaus massatehtaiden jätevesien ympäristövaikutuksista ja niiden suhteesta valkaisutekniikan kehitykseen. Viimeaikaiset tieteelliset selvitykset antavan aiheen olettaa, että AOX-kuormituksen pienentymisen yhteydessä usein tapahtuva samanaikainen orgaanisen aineksen kokonaiskuormituksen pienentyminen on ollut jätevesien vähentyneen toksisuuden ja ympäristövaikutusten todellinen syy. Uudenaikaisten tehtaiden (AOX alle 1.5 kg/t massaa) aiheuttamat toksiset vasteet ovat yleisesti ottaen vähäisiä eivätkä osoita vaihtelua suhteessa AOX-päästöihin. Tähän mennessä tehdyt tutkimukset eivät ole osoittaneet ECF- ja TCF-valkaisusta aiheutuvien jätevesien poikkeavan johdonmukaisesti toisistaan toksisuuden suhteen. Jätevesien ulkoinen puhdistus vähentää toksisia vaikutuksia. Nykyaikaisten valkaistua sulfaattimassaa tuottavien tehtaiden alapuolisissa vesistöissä tehtyjen viimeaikaisten kenttätutkimusten perusteella ei ole osoitettavissa mitään yleistä vaikutuskuvaa. Näyttää siltä, että uudenaikaisten tehtaiden ympäristövaikutuksia ei voida ennustaa tehtaan käyttämien valkaisujaksojen perusteella ja että ympäristövaikutusten arvioinnissa myös muut prosessit kuin valkaisu on otettava huomioon.	
Asiasanat	selluteollisuus, valkaisu, teollisuusjätevesi, ympäristövaikutukset	
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Julkaisun teema	ympäristönsuojelu	
Projektihankkeen nimi ja projektinumero	Happikemikaalien käyttöön perustuvan massan valkaisun ympäristövaikutuksia, nro XC 101	
Rahoittaja/ toimeksiantaja	Enso-Gutzeit Oy, Oy Finnish Peroxides Ab, Kemira Chemicals Oy, Kymmene Oy, Oy Metsä-Botnia Ab, Veitsiluoto Oy, Suomen ympäristökeskus	
Projektiryhmään kuuluvat organisaatiot	Enso-Gutzeit Oy, Oy Finnish Peroxides Ab, Kemira Chemicals Oy, Kymmene Oy, Oy Metsä-Botnia Ab, Veitsiluoto Oy, Suomen ympäristökeskus, Suomen Ympäristötutkijaryhmä Oy, Jyväskylän yliopisto, Keskuslaboratorio	
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Presentationsblad

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Publikationens titel	Effekter i vattenmiljö av avloppsvatten från framställning av blekt massa – en översikt	
Publikationens delar/ andra publikationer inom samma projekt	Tidigare har det utkommit fem publikationer inom detta projekt.	
Sammandrag	I denna rapport diskuteras miljöpåverkan av massakok- och blekprocesser mot bakgrund av den tekniska utvecklingen. Vetenskapliga bevis tyder på att reduktionen av totalt organiskt material i samband med reduktionen av AOX-utsläppen var den verkliga orsaken till minskad toxicitet och miljöpåverkan hos massaindustrins avloppsvatten. De toxiska responsen mot avloppsvatten från moderna fabriker (AOX-utsläpp under 1.5 kg/t massa) är i allmänhet svaga och uppvisar ingen variation kopplad till AOX-utsläppen. Varken ECF eller TCF blekkoncepten producerar avloppsvatten som konsistent skulle uppvisa lägre toxicitet i förhållande till varandra. Extern rening minskar toxiska effekter av avloppsvatten. Baserar på senaste fältundersökningar i recipienter utanför moderna sulfatmassafabriker är det inte möjligt att påvisa något allmänt effektmönster. Miljöpåverkan av moderna massafabriker kan inte förutsägas på basen av vilken bleksekvens som utnyttjas och vid framtida utvärderingar av fabrikens miljöpåverkan borde större uppmärksamhet fästas vid andra processer än blekningen.	
Nyckelord	massaindustri, blekning, industriavloppsvatten, miljöeffekter	
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ENVIRONMENTAL PROTECTION

The aquatic environmental impact of pulping and bleaching operations – an overview

The objective with the present report is to review the recent literature concerning environmental effects of pulp mill effluents in the light of introduction of new bleaching technologies. It is also the aim to see if and how the available scientific material supports the view that bleaching of pulp is responsible for the effects noted. Finally, gaps and areas for future research will be discussed.

This review is part of a broader project: "Environmental Impact of Oxygen Chemicals in the Bleaching of Kraft Pulp". The first phase of the project was initiated in 1993 and the second phase will end in 1997. The project is co-funded by Enso-Gutzeit Oy, Finnish Peroxides Oy, Kemira Chemicals Oy, UPM-Kymmene Oy, Oy Metsä-Botnia Ab, Veitsiluoto Oy and the Finnish Environment Institute. The project is coordinated by the Finnish Environment Institute in cooperation with the representatives from West and Southwest Finland Regional Environment Centres, the industry and the performing scientists.

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