BOREAL ENVIRONMENT RESEARCH 2: 239–246
Helsinki 11 November 1997

ISSN 1239-6095

Improved water quality by process renewal in a pulp and paper mill

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Kaplin, C., Hemming, J. & Holmbom, B. 1997. Improved water quality by process renewal in a pulp and paper mill. *Boreal Env. Res.* 2: 239–246. ISSN 1239-6095

The Kaukas pulp and paper mill on southern Lake Saimaa was investigated to evaluate the environmental benefits of process renewal, i.e. the substitution of chlorine by chlorine dioxide in the bleaching and the modernisation of the biological effluent treatment. A comparative study of the mill effluent and the catchment water area was performed before (1991) and after (1993/1995) the changes. The chemical composition of the mill effluent was analysed with special emphasis on chlorinated organics and wood extractives. The same compounds were analysed in lake waters with respect to distribution and persistence. The study revealed a considerable decrease in the concentrations of chlorinated organics both in the mill discharge and in the lake. Most wood extractives also decreased in the effluent. However, the discharge of some wood extractives, such as sitosterol, was not significantly affected by the changes.

Introduction

During the last ten years growing concern about possible environmental effects of organic compounds originating from pulp and paper mills has caused many mills to invest heavily in process renewal, aiming at improving the quality of the mill effluent. Consequently, it is important to follow up these changes and evaluate the outcome of this investment. In this work we report on chemical changes in both mill effluent and recipient water system after considerable process changes in a pulp and paper mill.

This study was part of a broader project, aiming at assessing the distribution and ecotoxicological impact of pulp mill effluents in the southern Saimaa lake systems. The aim of this study was to compare the effluents from the Kaukas mill in 1991, 1993 and 1995, and to compare the concentrations of selected chlorinated organics and unchlorinated wood extractives in the recipient system during the same period.

The mill

The Kaukas mill is a modern integrated pulp and paper mill. During the years of the study, 1991–1995, the pulp mill increased its production of bleached kraft pulp from about 350 000 t a^{-1} in 1991 to about 440 000 t a^{-1} in 1995. Both hardwood (mainly birch) and softwood (mainly pine) kraft pulp was produced in the ratio of approx. 60:40. The kraft pulp was used together with spruce groundwood pulp in the integrated paper mill at Kaukas for producing LWC and MFC magazine papers on two paper machines. The Kaukas mill complex also includes a large sawmill and a mill producing crude tall oil and sitosterol. The combined pulp and paper mill effluent, about 1.5 $m^3 s^{-1}$, is treated biologically and discharged into the recipient, which flows past the mill outlet at about 40 $m^3 s^{-1}$.

During the first sampling period (1991) the mill used traditional chlorine and chlorine dioxide bleaching. The sequence was D/C(EO)DED and the proportion of C was 5% and 45% of the active chlorine in the bleaching of hardwood and softwood pulp respectively. In 1992, the mill stopped using elemental chlorine (<< 1%), thus changing the bleaching sequences to OD(EO)D(EP)D for hardwood pulp and D(EOP)DED for softwood pulp (Table 1).

In 1991, the mill effluent was treated in an aerated lagoon system with a retention time of 3–4 days. Since April 1992 the effluent has been treated in a modern super low-loaded activated sludge treatment plant, incorporating an aerobic selector (Simpura and Pakarinen 1994).

These process changes have clearly improved the quality of the effluent discharged from the mill, measured by conventional effluent parameters (Table 2).

Methods

Water samples were taken of the treated mill effluent and of recipient waters over a period of 4–5 weeks in May–June 1991, 1993 and 1995. The recipient sampling sites were the same in 1991 and 1993, with one site upstream from the mill and eight sites below the mill. In 1995, some of the sampling sites were different, with two sites upstream from the mill and seven sites below (Fig. 1).

Table 1. Bleach stage designation.

C	Chlorine
D	Chlorine dioxide
E	Alkaline extraction
O	Oxygen
P	Peroxide

The mill effluent was sampled automatically at the outlet to the lake. Composite samples were analysed daily at the mill's laboratory for common wastewater parameters such as BOD, COD (Cr), pH, suspended solids, sodium and AOX (Adsorbable Organic Halogen). Weekly composite samples were stored separately in a freezer for further analysis.

Recipient watersamples were collected twice a week. The fresh samples were analysed for some general water quality parameters (pH, conductivity, sodium and chloride). The samples were frozen and kept in glass bottles at – 20 °C for transport to Åbo Akademi. AOX analysis of the recipient water was made at the Kaukas mill laboratory by the SCAN standard method (SCAN-W 9:89).

Before analysis the samples were combined into 30-day samples to obtain one composite sample representing the average of each sampling site over the sampling period. Analyses for chlorinated phenolics and for wood extractives were made by gas chromatography after extraction and derivatisation.

Chlorophenolic compounds were analysed by GC with EC detector after extraction with hexane. Free chlorinated phenolics were analysed after *in situ* acetylation (NCASI method CP-86.01) while the determination of total chlorinated phenolics required hydrolysis for 16–18 h at 70 °C in a 2.5 M KOH solution of 50% ethanol. 2,6-dibromophenol was used as an internal standard for chlorinated phenolic compounds.

Lipophilic wood extractives in lake water samples were analysed after filtration (GF/A glass fibre filter, approx. 1–10 µm) separately on the solid matter and the filtrates. Solid matter was hydrolysed for 2 h at 70 °C in 2 ml of a 0.5 M KOH solution of 90% ethanol and then diluted and extracted with 3 portions of 6 ml diethyl ether. Approx. 1 l of filtrate was passed through an XAD-8/XAD-2 column (80:20 ratio) and absorbed lipophilic material was eluted by diethyl ether. Heptadecanoic acid was added as an internal standard and all extracts were methylated by diazomethane and, furthermore, silylated before analysis by GC with FI detector. Effluent waters were filtered and the particles were subjected to the same analyses as the particles in the lake water samples. Further, 100 ml of the filtrate was acidified (pH ~ 3) and extracted twice with equal

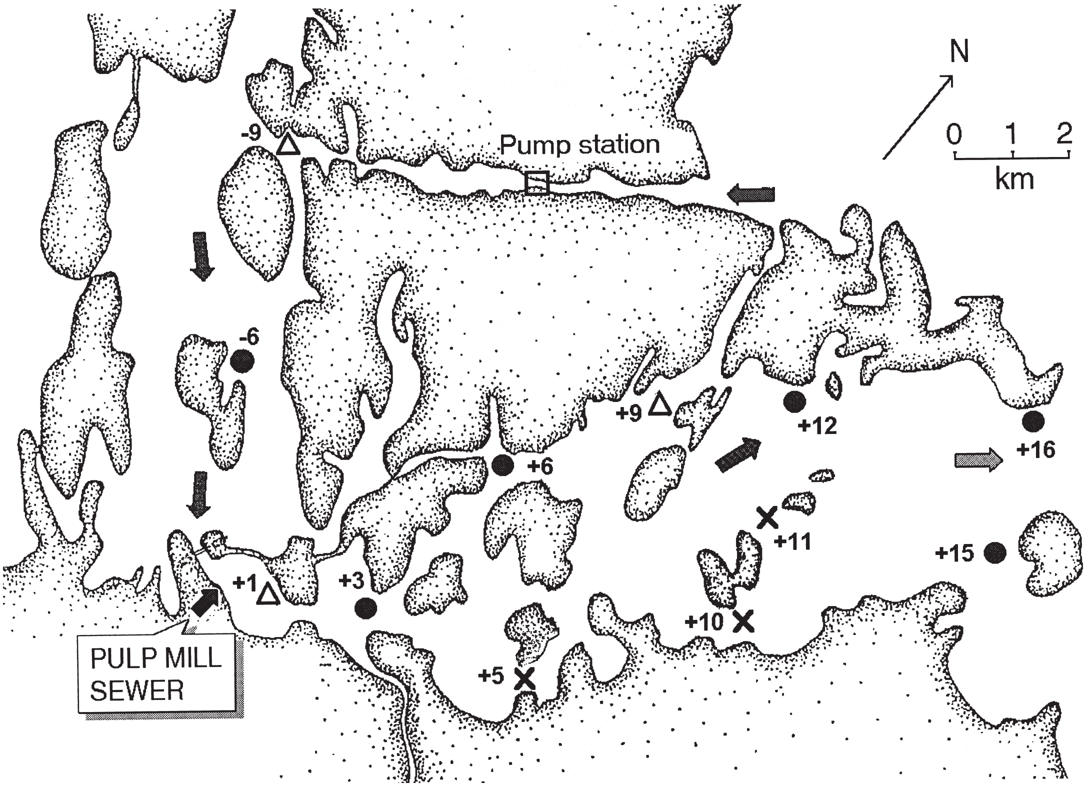

Fig 1. Map of the receiving water area with water flow directions and sampling sites. The numbers refer to the approximate distance (km) from the mill. Sampling sites marked ● were used in all three sampling periods. Sites marked × were sampled in 1991 and 1993. Sites marked Δ were sampled only in 1995.

amounts of MTBE. Heptadecanoic acid was added as an internal standard. After evaporation the extracts were derivatised and analysed as above.

TOC (Total Organic Carbon) was measured with a Shimadzu TOC 5050 and absorbance was determined with a Perkin-Elmer UV/VIS spectrophotometer at three different wavelengths: 200, 254 and 460 nm.

Results and discussion

The general water parameters showed similar trends in both the effluent water and the receiving water samples (Table 3). The sodium concentrations and conductivity values (not shown) were approximately the same for all sampling periods at each sampling point. However, the chloride

Table 2. Yearly average values for standard effluent parameters for the Kaukas Mill.

		1990	1991	1992	1993	1994	1995
BOD	$t\ d^{-1}$	12.5	14.3	8.4	1.7	1.4	1.5
COD	$t\ d^{-1}$	90.1	99.2	55.6	38.6	35.3	40.0
Suspended solids	$t\ d^{-1}$	9.3	9.6	4.6	3.4	2.7	n.a.
AOX	$t\ d^{-1}$	1.8	1.7	0.4	0.4	0.3	0.4
Phosphorus	$kg\ d^{-1}$	123	111	58	34	20	23
Nitrogen	$kg\ d^{-1}$	n.a.	1 272	598	405	307	353

n.a.= not analysed.

content of the effluent had decreased substantially from 1991 to 1993, and the decrease was even more pronounced in the AOX content. A similar decrease in chloride and AOX content after 1992 could be seen at all sampling sites below the mill. At the reference sites upstream from the mill no significant change in these parameters was evident over the study period. Although both the AOX and the chloride concentrations decreased after the process changes in 1992, slightly elevated concentrations compared to the reference sites were still found in the recipient below the mill (Fig. 2). In 1993, an increase in AOX 10–12 km downstream from the mill indicated some other source of organic halogen pollution than the pulp mill. The fact that other parameters, such as TOC and chloride concentration, did not exhibit a similar peak at this distance, supports this assumption.

The TOC values also decreased after the process changes, especially at the sampling sites close to the mill. Further away (< 10 km) the concentration had almost fallen to that of the reference sites and the differences between the sampling years or sampling sites were small. Values for light absorbance followed the same trend as the TOC values. The absorbance values measured at 460 nm represent the colour of the water sample. The process changes reduced both colour emissions and the discharge of organic compounds. This is in accordance with previous studies showing that both chlorine dioxide substitution (Pryke *et al.* 1994) and activated sludge treatment of effluents (Kukkonen and Välttilä 1988) will decrease effluent colour.

Lipophilic components in effluent

The chlorophenolic compounds were almost eliminated from the effluent by the mill's conversion to chlorine dioxide in 1992. In 1991, the concentration of the predominant chloroguaiacol, 345-CG, was 140 μg l^{-1} whereas in 1993 the concentration was as low as approximately 1 μg l^{-1} in the effluent. The other components showed about the same magnitude of decrease and the total concentration of measured chlorophenolic compounds decreased from about 350 μg l^{-1} in 1991 to less than 10 μg l^{-1} in 1993 and 1995. This elimination of chlorophenolic compounds from pulp mill effluents by substituting chlorine dioxide for elemental chlorine has been documented in previous studies (Dahlman *et al.* 1993, Pryke *et al.* 1994).

The distribution pattern between different chlorophenolic compounds remained more or less the same with the exception of a slight change

Table 3. Values for standard water quality parameters of water samples at the sampling sites and for mill effluent during the study. The values are an average for the 30-day sampling periods. The site numbers refer to the distance from the mill (km).

Sampling site	Na (mg l^{-1})			TOC (mg l^{-1})			AOX (μg l^{-1})			Cl (mg l^{-1})		
	1991	1993	1995	1991	1993	1995	1991	1993	1995	1991	1993	1995
P-9	n.a.	n.a.	2.9	n.a.	n.a.	9.6	n.a.	n.a.	20	n.a.	n.a.	3.6
P-6	2.9	2.9	3.1	6.9	7.1	9.8	40	30	30	4.3	3.5	3.8
Mill effl.	231	247	264	200	85	112	16 300	2 070	3 020	264	153	148
P+1	n.a.	n.a.	17.0	n.a.	n.a.	13.2	n.a.	n.a.	140	n.a.	n.a.	10.6
P+3	13.1	11.9	14.2	22.9	9.3	13.3	520	90	130	18.1	8.2	9.2
P+5	12.7	10.7	n.a.	12.2	9.1	n.a.	540	80	n.a.	16.4	7.3	n.a.
P+6	12.9	10.8	12.5	11.5	9.1	12.5	540	80	110	16.9	7.3	8.8
P+9	n.a.	n.a.	10.7	n.a.	n.a.	14.5	n.a.	n.a.	90	n.a.	n.a.	7.7
P+10	11.3	9.6	n.a.	10.5	8.8	n.a.	420	90	n.a.	14.7	6.7	n.a.
P+11	8.6	8.0	n.a.	8.8	8.3	n.a.	250	110	n.a.	11.4	6.1	n.a.
P+12	8.9	8.0	8.0	9.4	8.6	10.6	190	180	60	11.6	5.9	5.9
P+15	6.9	6.6	7.0	9.3	8.5	9.9	210	60	60	9.1	5.2	5.4
P+16	6.8	6.1	7.0	8.1	8.0	12.4	680	50	60	8.9	5.0	5.4

n.a.= not analysed.

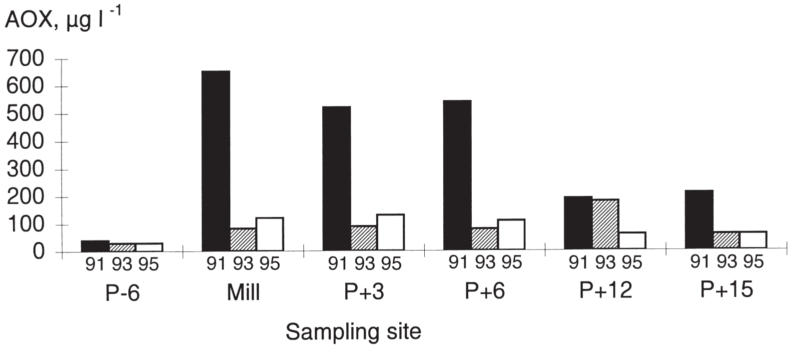

Fig 2. AOX concentrations at sampling sites in 1991, 1993 and 1995. The value at "Mill" is the effluent value corrected for a theoretical dilution of 4% at the discharge point.

towards compounds with lower degrees of chlorination. In 1995, neither tetrachloroguaiacol nor tetrachlorocatechol could be detected in the effluent (Table 4). Since highly chlorinated compounds are generally more toxic and less degradable than those with lower degrees of chlorination, the change towards less chlorinated compounds is a positive one.

Chlorinated guaiacols were the predominant compound group while chlorinated phenols showed the lowest concentrations as a group.

Contrary to the chlorinated compounds, wood extractives are not formed in the process, but enter the mill as part of the raw material. Nevertheless, wood extractives are receiving more and more attention today since natural wood constituents are thought to be responsible for most of the acute toxicity of modern ECF- and TCF-bleached pulp effluents (Verta *et al.* 1996). Most (60–90%) of this toxicity has been attributed to resin acids (Stuthridge *et al.* 1995).

The concentration of wood extractives in the mill effluent also decreased substantially after the process changes in 1992 (Fig. 3). This is obviously due to the new, modern activated sludge plant installed in 1992 since modern biological treatment plants are very effective in removing wood extractives (Liu *et al.* 1996). In 1995 the concentrations of fatty and resin acids were slightly higher than in 1993, but they were still clearly below the concentrations measured in 1991. For sterols and the birch bark-derived betulinol, however, no significant decrease could be seen in effluent waters during the study period.

Oleic acid is the dominating fatty acid in the effluent. Also palmitic acid has shown relatively high concentrations. The same components dominated the fatty acids both before and after the changes. Dehydroabietic acid showed the highest concentrations of resin acids in 1991. The second highest concentration was that of abietic acid but it was less than half of the concentration of dehydroabietic acid. In 1993 and 1995 no single resin acid dominated, the resin acids with the highest concentrations were pimaric acid, isopimaric acid and dehydroabietic acid.

Table 4. Total chlorinated phenolics in the Kaukas Mill effluents in 1991, 1993 and 1995. The distribution between highly chlorinated and less chlorinated compounds is also shown. Monochlorinated guaiacols or catechols were not determined. In 1991 chlorophenols were determined as a group.

	1991	1993	1995
Chlorophenols (µg l^{-1})			
monochlorinated		n.a.	1.8
dichlorinated		n.a.	0.0
trichlorinated		0.08	0.3
tetrachlorinated		0.38	0.4
pentachlorinated		0.06	0.0
Total chlorophenols	**15**	**0.52**	**2.5**
Chloroguaiacols (µg l^{-1})			
dichlorinated	82	1.7	0.5
trichlorinated	163	1.3	4.2
tetrachlorinated	46	0.1	0.0
Total chloroguaiacols	**291**	**3.1**	**4.7**
Chlorocatechols (µg l^{-1})			
dichlorinated	0.0	0.25	0.10
trichlorinated	45	0.35	0.25
tetrachlorinated	8.9	0.44	0.0
Total chlorocatechols	**54**	**1.0**	**0.35**

n.a. = not analysed.

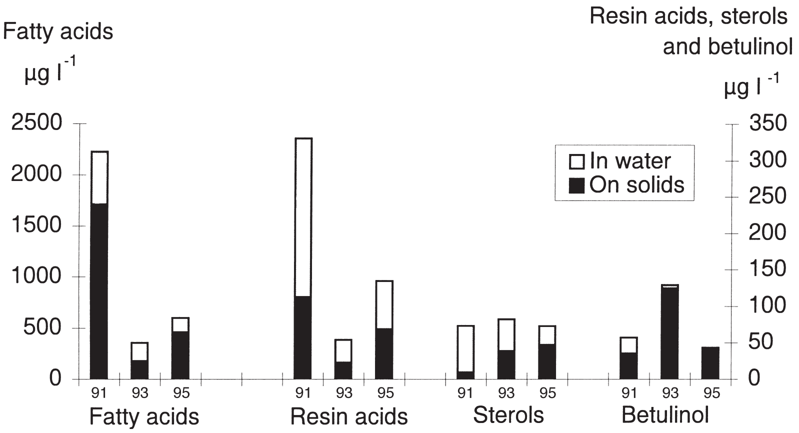

Fig. 3. Wood extractives in mill effluents. The scale on the left refers to fatty acids while resin acids, sterols and betulinol are shown in the righthand scale.

Lipophilic components in the receiving waters

As expected, the radical drop in discharge of chlorinated compounds was observed in the recipient concentrations too. The total concentrations of chlorophenolics decreased by more than 95% at most sampling sites. In 1991, a clear gradient was noticed over the study area, but this was not seen in 1993 or in 1995. In fact, no significant difference could be found between the concentrations at the reference sites and at downstream sampling sites. Also, the reliability of individual analytical results was lower in 1993 and in 1995 since the concentrations approached the analytical detection limit.

The concentrations of wood extractives in the lake waters were rather similar during the 1993 and 1995 study periods, although the concentrations in the effluent changed slightly (Table 5). Also, the distribution between different wood extractives remained about the same during the study. Among fatty acids the dominating components were acids with 18 carbon atoms, i.e. oleic, linoleic and stearic acids. Palmitic acid (16 carbon atoms) was also found in relatively high concentrations. The same acids dominated in the effluent and in the receiving waters. They were, however, present also at the reference sites at almost the same concentrations as at downstream sampling sites. The influence of the mill as a source of fatty acids for the lake system is therefore rather small. The same is true for resin acids.

Table 5. Concentrations of wood extractives in lake waters in 1993 and 1995.

Sampling site	Fatty acids (µg l^{-1})		Resin acids (µg l^{-1})		Sterols (µg l^{-1})		Betulinol (µg l^{-1})	
	1993	1995	1993	1995	1993	1995	1993	1995
P-6	30.7	31.2	3.1	1.2	6.1	2.3	0.3	1.4
P+1	n.a.	40.1	n.a.	2.9	n.a.	5.5	n.a.	4.6
P+3	43.9	35.2	3.6	2.4	11.2	4.8	3.3	0.8
P+5	41.3	n.a.	10.0	n.a.	10.5	n.a.	2.1	n.a.
P+6	43.0	39.9	7.0	2.2	10.0	10.4	2.1	1.3
P+9	n.a.	39.7	n.a.	1.8	n.a.	4.5	n.a.	0.0
P+10	39.9	n.a.	7.8	n.a.	8.5	n.a.	1.4	n.a.
P+11	43.0	n.a.	9.7	n.a.	10.1	n.a.	0.6	n.a.
P+12	45.4	41.4	12.7	1.2	11.1	3.6	0.5	0.0
P+15	37.4	36.8	5.6	1.4	8.1	4.0	0.3	0.9
P+16	34.8	43.0	4.3	1.3	6.9	4.1	0.5	0.0

n.a.= not analysed

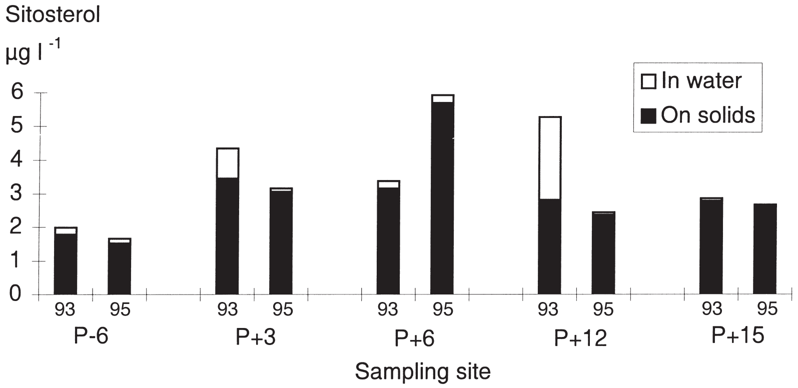

Fig 4. Sitosterol concentrations at sampling sites in 1993 and 1995.

They were found in the effluent and in the receiving waters at almost the same concentrations as at the reference sites. A small increase in the concentrations after the mill is evident but no clear gradient could be seen. It should be noticed that the lake system of southern Saimaa is influenced by several pulp and paper mills as well as by municipal sewage, and it is likely that some components circulate even to the "clean" reference sites.

The only components showing a clear increase in concentration below the mill were sterols and betulinol. Several sterols originating from the mill were detected, sitosterol being the dominating one. The sitosterol concentrations were about twice as high below the mill compared to the reference sites above the mill. Betulinol, originating from birch bark, showed an even larger increase. In 1993 the concentration of betulinol close to the mill was more that ten times as high as the concentration at the reference site. The sitosterol concentrations decreased slowly in the recipient (Fig. 4). Hence concentrations at the furthest sampling sites (15–16 km below the mill) were still slightly higher than those at the reference site. Betulinol, however, was removed from the water quite quickly. The concentrations 15–16 km below the mill were the same as at the reference site. The reason could be its strong association to particles. More than 95% of the betulinol in the samples was bound to suspended particles and might therefore be distributed to the sediments. Although sitosterol also showed a strong adsorption to particles it could be found in the water phase too.

Wood extractives in general seem to be to a great extent absorbed by suspended particles in the water. This naturally affects their bioavailability.

Conclusions

The replacement of chlorine by chlorine dioxide during pulp bleaching in combination with efficient secondary effluent treatment at the Kaukas mill has resulted in almost complete elimination of highly chlorinated compounds in the mill effluent. The AOX discharges decreased significantly as did the TOC content and the colour of the effluent. The new activated sludge treatment is more efficient in removing fatty and resin acids, but sterols and betulinol seem unaffected by the changes.

The reduction in the concentration of chlorophenolic compounds in southern Lake Saimaa after process alterations implemented in spring 1992 has been noticeable. Also the overall concentration of wood extractives in the lake area has decreased, although the concentrations of some individual compounds seem unaffected by the changes. This has resulted in a recovery of the Lake Saimaa ecosystem in the sense of reduced exposure (Oikari and Holmbom 1994). Studies of whitefish in the same area show a consistent change in some biomarkers used (Petänen *et al.* 1996).

However, monitoring and further investigations into some wood extractives are still needed. For example, sitosterol, which has recently been suggested to cause reproductive dysfunction in fish (Mellanen *et al.* 1996), is not as efficiently removed during effluent treatment as resin acids and could be inhibiting the recovery of the fish population in lake areas receiving pulp and paper mill effluents. Also, although not reported here, monochlorovanillin is known to be formed in ECF-bleaching (O. Dahlman pers. comm.).

In conclusion, the process changes implemented at the Kaukas Mill have greatly improved the quality of the mill effluent and also that of the receiving lake system.

Acknowledgements: This investigation was supported by Kymmene/Kaukas Corp., the Maj and Tor Nessling Foundation and the Academy of Finland. We also thank personnel at Saimaan Vesiensuojeluyhdistys, Lappeenranta and Kaukas Mills for sampling, standard water analyses and technical support. We are grateful to Dr. Aimo Oikari and Dr. Jussi Kukkonen for fruitful cooperation, and to Frank Vikström for laboratory analyses.

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Received 13 March 1997, accepted 2 May 1997