

The characterization of dissolved organic matter in pulp and paper mill effluent streams and the effect of treatment on the quantity and quality of organic matter

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Abstract

Pulp and paper mill effluents are heterogeneous of their origin and composition. The analytical methods which are used in order to characterize the organic matter provide just limited information of the nature of the organic matter (SS, TOC, COD, BOD) or they are very selective, laborious and expensive (e.g. GC/MS). Size exclusion chromatography was used to assess the concentration of dissolved organic matter and molecular size distribution of the various effluent streams in a mechanical pulp and paper mill. Particular attention was paid to the transformation of dissolved organic matter during the primary, secondary and tertiary treatment stages of waste water treatment. According to the conventional analyses the removal efficiencies were COD and BOD were 85 and 99 percent, respectively. The HPLCSEC method indicated much lower removal efficiencies for dissolved organic carbon removal. The method is simple, rapid and widely used in drinking water treatment plants but needs further testing and modification for forest industry effluents.

Keywords: Forest industry, waste water, dissolved organic matter, characterization, size exclusion chromatography

Introduction

Pulp and paper industry effluent contains organic matter from various sources. The high molecular size organic matter is originating from the raw material, wood and its constituents. The molecular size of dissolved organic matter ranges from hundreds of Daltons to several tens of thousands. There are also organic compounds originating from the process chemicals, fillers and coating mix such as polyacrylate, organic acids, carboxymethylcellulose and starch (Linhart et al. 1987).

In mechanical pulping most of the wood is utilized as pulp but still some of the raw material ends up to waste water. Mechanical pulp effluent contains particularly hemicelluloses, lignin like compounds, sugars, and organic acids and less water soluble compounds such as cellulose and its derivatives and extractives. (Holmbom 1999)

Concentration of organic matter in waste water of forest industry has been traditionally measured by oxidizing the organic matter by oxidation of the organic matter by strong acid, Potassium Dichromate, (Chemical Oxygen Demand, COD) or microbiologically (Biologically Oxygen demand, BOD). The hindsight of BOD is that it requires significant work and expertise, results can be obtained not sooner than after one week and the analyze itself is sensitive to toxic compounds. Total organic carbon, TOC, which is based of total combustion of organic matter, is also widely used. Separate compounds have been identified by using different chromatographic techniques followed by UV (Holmbom 1999) mass selective detection techniques (Voss and Rapsomatiotis 1985), or other detection methods. Different kind of oxidative and pyrolytic techniques are used to release

characteristic fragments from the high molecular mater of wood origin (Hyötyläinen et al. 1995, 1998). High pressure liquid chromatography, HPLC, has been used to analyze of cellulose and its derivatives but after derivatization and by using organic solvents (Erameeva 2003). Aqueous based eluents such as NaOH and Sodium acetate are more suitable for hemicelluloses and organic acids (Erameeva and Bykova 1998). In this study HPLC combined to Size Exclusion Chromatographic column (HPLC-SEC) with acetate buffer and UV detection, was used to characterize the dissolved organic matter in different effluent streams of pulp and paper mill. Particularly the change of organic matter profile in different stages of waste water treatment train was monitored. Size-exclusion chromatography has been widely used for the analyses of polymeric matter (Erameeva 2003) and lignin like humic matter in various water (Matilainen et al. 2002, Knuutinen et.al 1988, Vartiainen et al. 1987) and wastewater streams (Haapea et al. 2002). The method has proven to be particularly useful in order to screen the changes in the composition of dissolved organic matter during the treatment train due to the chemical, physical and biological processes. It has not been used so far for the characterization of the forest industry effluents and for the monitoring of their treatment The aim of this work was to test the suitability of aqueous HPLC-SEC method for the monitoring of purification process and to give more information of the removal of organic matter than the traditional parameters BOD, COD or COD/BOD – ratio can provide.

Materials and methods

Sampling sites and procedures

The experimental part of this study was carried out at a Finnish pulp and paper mill. The mill is located in southern Finland and it produces wood-containing printing papers with three paper machines. The mechanical pulp used in the paper-making process is produced at the mill. The types of pulp produced are Pressurized Refined Mechanical Pulp and Ground Wood. Both processes use spruce as raw material. The most significant source of organic wastewater load is the pulp production.

The examined waters were sampled from different stages of mechanical pulping and wastewater treatment process. The effect of mechanical and biological wastewater treatment was studied as well as the chemical tertiary treatment. The schematical layout of the process can be seen in Figure 1.

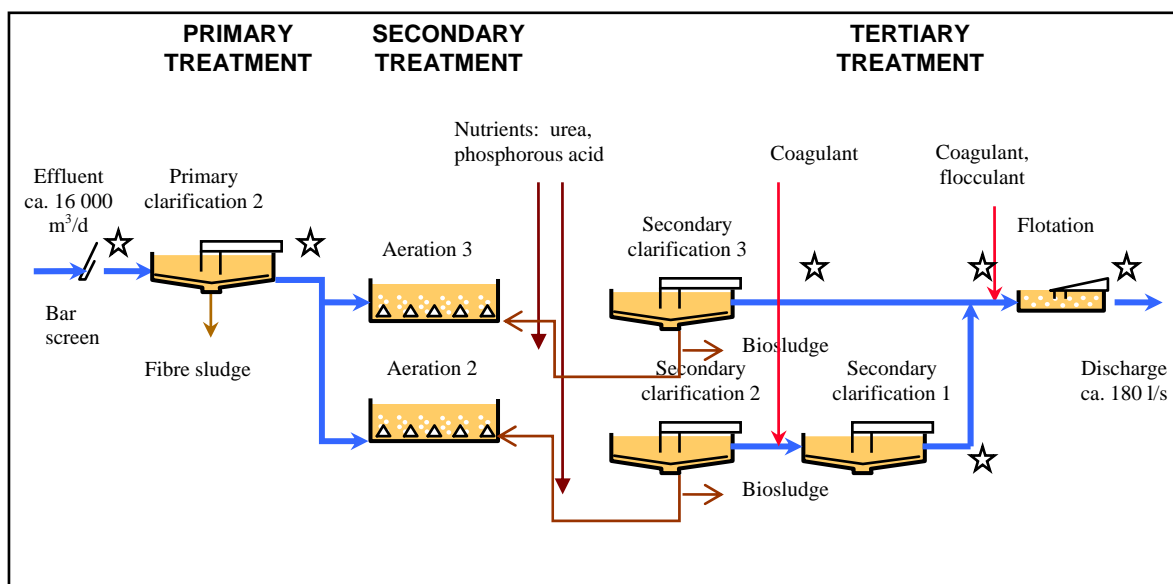


Figure 1. Wastewater treatment plant at the pulp and paper mill. Sampling positions at the treatment plant are marked with a star. Other five samples were taken from the production sections of the mill from wastewater channels.

Analyses

COD was analyzed by Dr Lange Potassium dichromate method. BOD₇ was determined by a method based on the SFS 5508:1991 standard. Suspended solids were analyzed according the SFS 3037 standard by using Whatman GF/A filters.

Size-exclusion chromatography method followed the procedure widely used for the characterization of surface waters containing humic compounds (Knuutinen et al. 1988, Vartiainen et al. 1987). The liquid chromatography equipment was Hewlett Packard 1100 Series. The column used was TSK-gel G3000SW 7,5 x 30 cm (Tosoh Bioscience) and eluent was 0,01 M Sodium acetate solution. Flow rate was 1 ml/min. The samples were filtrated by 0,45 µm Pall Life Science IC Acrodisc syringe filter after dilution of the samples to 1:10 by Milli-Q water. The detector was Hewlett Packard UV/Vis series diode array detector and the detection wavelength was 254 nm. The chromatograms were integrated by ChemStation program. The heights of the peaks were used for data analysis.

Results and discussion

The concentration of SS, COD, BOD and HPLC-sec in different effluent streams

The concentration of SS, BOD, COD and the BOD/COD –ratio in the different effluent streams and in different stages of waste water treatment process are presented in the Table 1. Besides of the average value of four sampling periods also the minimum and maximum concentrations are presented.

Table 1. Characteristics of different wastewater fractions during the monitoring.

	SS			COD _{Cr}			BOD ₇			BOD ₇ /COD _{Cr} -ratio		
	\bar{x}	mg/l min	max	\bar{x}	mg/l min	max	\bar{x}	mg/l min	max	\bar{x}	min	max
Debarking	1959	1313	2366	2858	2508	3684	1215	960	1700	0.42	0.38	0.46
Refining	956	450	1384	2507	1657	3017	1033	640	1500	0.42	0.37	0.50
Specialty pulp production	221	72	454	5175	2585	7574	2100	1200	2600	0.43	0.33	0.48
Wastewater channel 1	1326	411	2285	3057	2310	3857	1267	1000	1400	0.42	0.36	0.47
Wastewater channel 2	1617	819	3242	1372	1087	1511	628	390	840	0.45	0.36	0.56
Feed to primary clarification	2351	731	5166	1466	1027	1738	707	560	820	0.44	0.38	0.47
Primary clarified wastewater	133	100	162	1761	1607	2081	755	720	800	0.43	0.38	0.47
Secondary clarified wastewater 1/2	94	41	156	263	218	280	4.0	3.1	5.8	0.01	0.01	0.02
Secondary clarified wastewater 3	73	53	118	271	245	307	5.4	3.7	6.9	0.02	0.01	0.02
Feed to chemical treatment	87	53	118	258	236	276	5.2	4.1	6.4	0.02	0.02	0.02
Discharge	129	97	150	223	202	244	4.6	3.0	7.2	0.02	0.01	0.03

The most concentrated effluent originated from the debarking and specialty pulp production. The volumes of those streams are relatively low and the effluents are diluted when they enter to the treatment plant. The suspended solids were removed in the primary clarification with 95 percent efficiency but there was hardly any removal of BOD or COD. The organic matter, measured as BOD and COD, was removed in the activated sludge treatment with 99 and 85 percent efficiency, respectively. The removal of any organic matter could not be detected in the tertiary treatment. It is meant mainly for the phosphorous removal (data not shown). The BOD/COD- ratio dropped from 0,44 to 0,02 in the biological treatment stage, which indicates that there was hardly any biologically degradable matter left in the treated effluent although the COD concentration was still over 200 mg/l. Residual organic matter which is difficult to be removed by conventional treatment techniques is called refractory organic substances (Hesse 1999).

SEC –results

Molecular size distribution of debarking, specialty pulp production and refining effluent fractions are presented Figures 2–4. Figure 5 depicts the chromatogram of primary clarification feed water which represent all wastewater fractions produced in the mill.

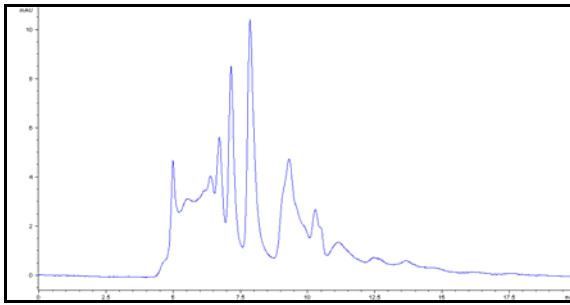


Figure 2. HPSEC-chromatogram of debarking effluent. Y-axis 0...10 mAU. Sampling date 4.8.2005.

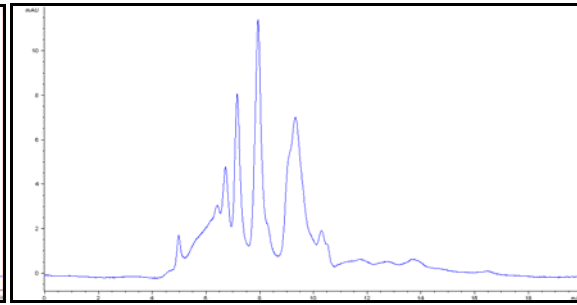


Figure 3. HPSEC-chromatogram of refining effluent. Y-axis 0...12 mAU. Sampling date 4.8.2005.

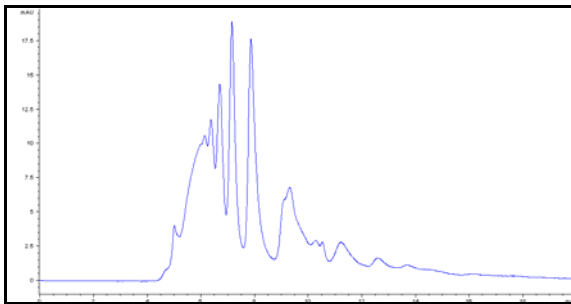


Figure 4. HPSEC-chromatogram of specialty pulp production effluent. Y-axis 0...18 mAU. Sampling date 4.8.2005.

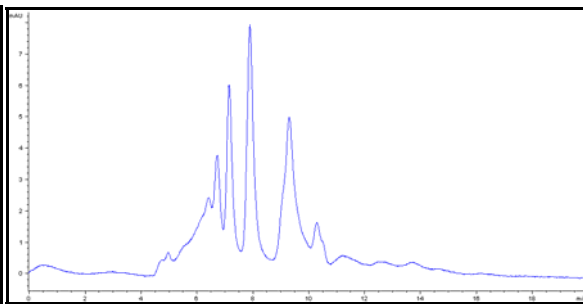


Figure 5. HPSEC-chromatogram of primary Clarification feed water. Y-axis 0...8 mAU. Sampling date 4.8.2005.

The chromatograms of debarking and refining effluents contain virtually peaks with similar retention time. However, the share of largest organic matter is bigger in debarking effluent sample than in refining effluent. The chromatogram of specialty pulp production effluent also included mainly same peaks as other effluent fraction from the production section but in different proportions. Especially the largest organic matter is present in quite large proportion. The primary clarification feed water is a combination of all the wastewater produced in the mill. It should be noticed when observing Figures 2-5 that the scale of y-axis is different in each Figure.

The change of dissolved organic matter molecular size distribution in the biological treatment can be seen in Figure 6. Blue line indicates the untreated effluent after primary sedimentation and the red and green lines are treated effluent after the secondary sedimentation. The green line comes from waste water channel after one sedimentation tank and red one after two sedimentation tanks in series with an additional chemical precipitation.

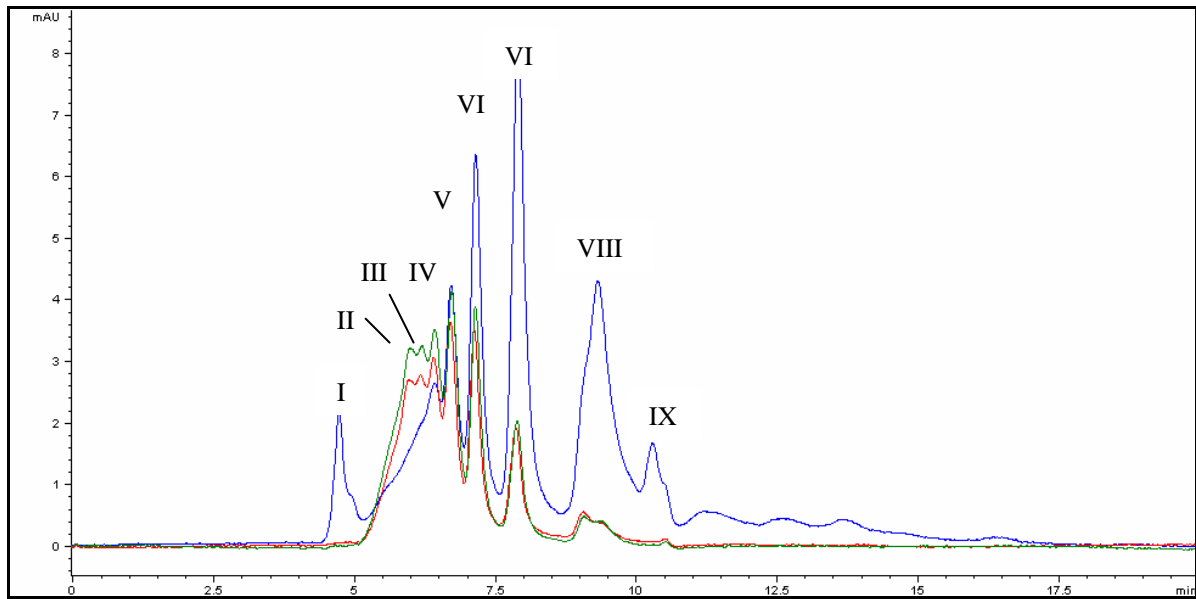


Figure 6. HPSEC-chromatograms of primary (blue) and secondary clarified (green and red) wastewater. The difference between the secondary clarified waters is due to additional chemical treatment in the other treatment line. Sampling date 4.8.2005.

The overall removal of dissolved organic matter during the secondary treatment, measured as the total peak high, was 28 percent. The highest molecular matter (peak I) was removed completely in the biological treatment stage as well as the smallest fractions. The intermediate size fractions VI and VII were removed 28 and 68 percent, respectively. There was, however, formation of high molecular matter (peaks II, III IV and V). This matter seemed to be removed in the secondary clarification with chemical (aluminum sulfate) addition (red versus green lines) to some extent measured as the sum of the peak heights (12 %) since there peaks are lower after two stage sedimentation.

Tertiary treatment

The behavior of dissolved organic matter in the tertiary treatment can be seen in the Figure 7. The blue line represents waste water from secondary clarifier and red line is waste water from dispersed air flotation. The peaks II, III and IV are removed from 16- 19 percent.

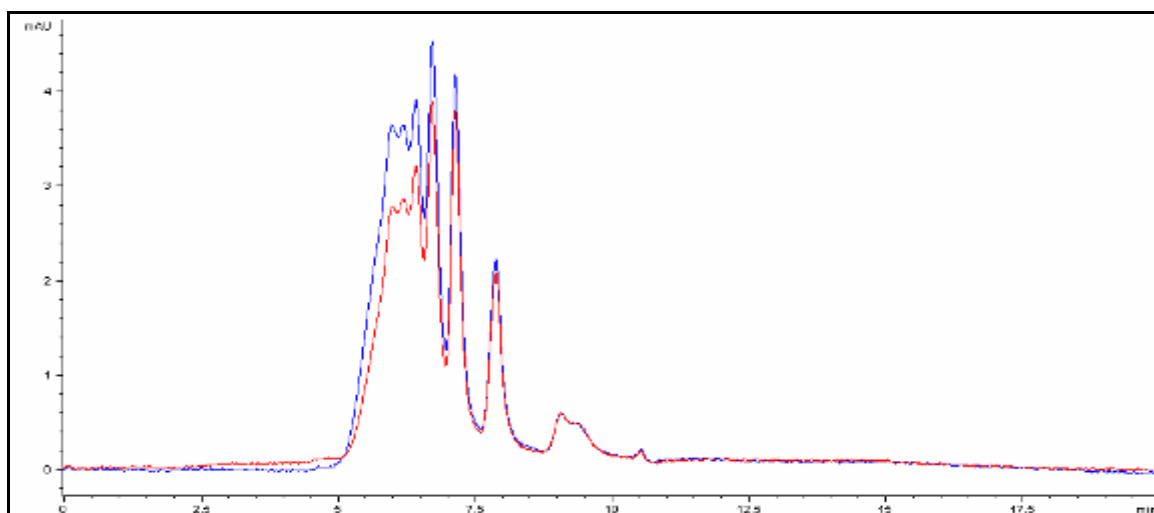


Figure 7. HPSEC-chromatograms of secondary clarified (blue) and chemically treated (red) wastewater. Sampling date 4.8.2005.

The height of total peaks and the partitioning of organic matter into different size fractions can be seen in Figure 8. Large (peak I), largish (peaks II–IV), intermediate (V–VII) and small molecular matter (VIII–).

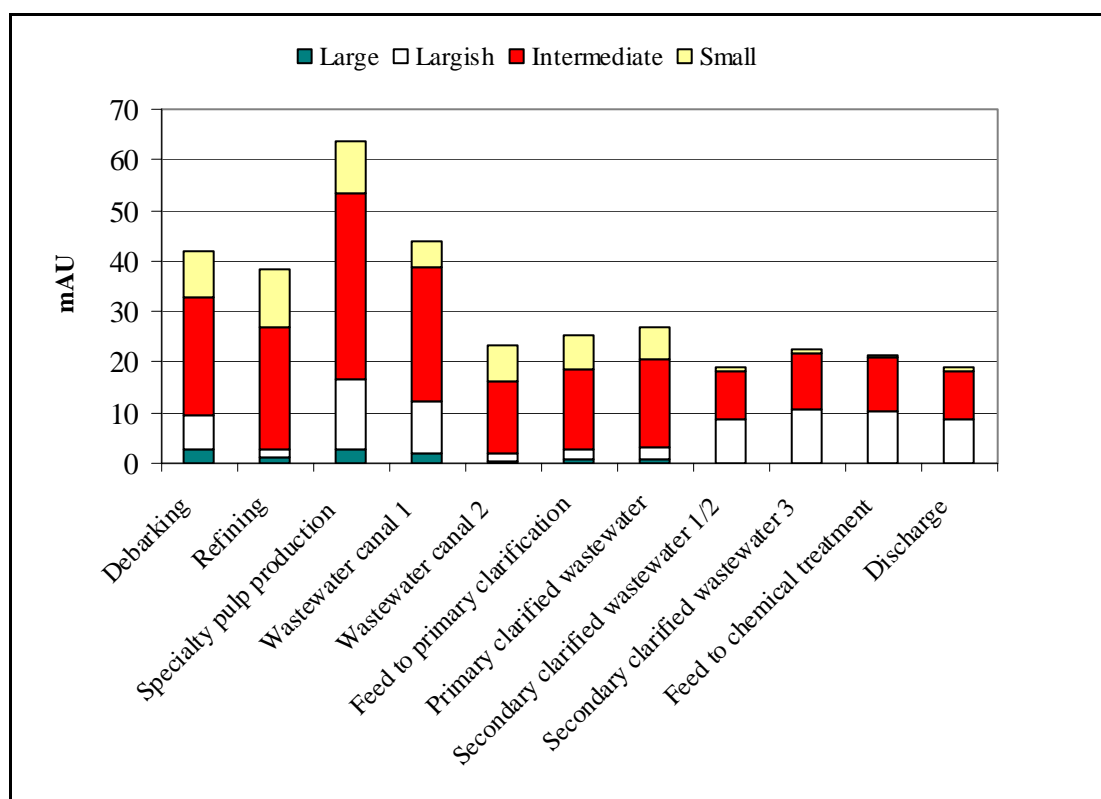


Figure 8. The shares of different molecular size classes in the monitored water fraction. When calculating the shares the medians of four samples were used.

The primary mechanical treatment didn't have any significant effect on the amount of dissolved organic matter measured as the sum of the peak heights. The activated sludge process, however, changed the chromatogram peak pattern by removing fractions from both ends of the molecular size range. Both the fraction with smallest molecular size and the fractions with largest molecular size were eliminated. The removal of intermediate size fraction varied from 5 to 74 percent. There was a formation of new large molecular size matter in the activated sludge treatment, which was later on partially removed by the chemical tertiary treatment.

Conclusions

The constant monitoring of waste water streams and the removal of organic matter in the different stages of waste water treatment train is necessary for the process control and for the optimization of purification results. Traditional parameters such as BOD, COD and the ratio of BOD/COD are traditionally used, but they provide just limited amount of information. BOD and BOD/COD -ratio indicates the organic matter, which is susceptible to biological degradation. Size-exclusion chromatography, SEC, gives an estimation of the amount and the characteristics of dissolved organic matter. It is a simple and rapid method, which is widely used in the characterization of raw waters and removal of organic matter in drinking water treatment plants. Combined to the concentration of residual COD it provides a tool to characterize the recalcitrant fraction of the remaining dissolved organic substance in the treated wastewater. The wider use of HPCL-SEC method requires still further testing and

optimization of the eluent composition and ionic strength and the calibration of molecular size distribution. However, it seems to be applicable method also for forest industry effluents.

Literature cited

Eremeeva, T., (2003) Size-exclusion chromatography of enzymatically treated cellulose and related polysaccharides: a review. *Journal of Biochemical and Biophysical Methods*, **56**, 253-264.

Eremeeva, T.E., Bykova, T.O., (1998) SEC of mono-carbomethyl cellulose (CMC) in a wide range of pH; Mark-Houwink constants, *Carbohydrate Polymers*, **36**, 319-326.

Hesse, S., Kleiser, G., Frimmel (1999), *Water science and Technology*, **40**, 1-7.

Holmbom, B., (1999) Analysis of papermaking process waters and effluents. In: Sjöström, E., Alen, R., (eds) Analytical methods of wood chemistry, pulping and papermaking. 1999. Springer series in wood science. pp. 269-285.

Haapea, P., Korhonen, S., Tuhkanen, T., (2002) Treatment of industrial landfill leachates by chemical and biological methods: ozonation, ozonation + hydrogen peroxide, hydrogen peroxide and biological post treatment for ozonated water, *Ozone Science and Engineering*, **24**, 369-378.

Hyötyläinen, K., Knuutinen, J., Malkavaara, P., (1998) Transport of high molecular mass lignin material in the receiving water system of a mechanical pulp mill, *Chemosphere*, **36**, 577-587.

Hyötyläinen, J., Knuutinen, J., Vilen, E., (1995) Characterisation of high molecular mass fraction of receiving water and sediments of a pulp mill by CuO-oxidation and HPLC, *Chemosphere*, **30**, 891-906.

Knuutinen, J., Viikki, P., Mannila, P., Mikkelsen, J., Paasivirta, J., Herve, S., (1988) High performance liquid chromatographic study of dissolved organic matter in natural waters, *Water Research*, **22**, 985-990

Linhart, F., Auhorn, W.J., Degen, H.J. ja Lorz, R. (1987) "Anionic trash": controlling detrimental substances. *Tappi Journal*, **70**, no. 10. 79-85.

Matilainen, A., Lindqvist, N., Korhonen, S., Tuhkanen, T., (2002), Removal of NOM in different stages of water treatment processes, *Environment International*, **28**, 457-465.

Vartiainen, T., Liimatainen, A., Kauranen, P., (1987) The use of TSK size exclusion column in determination of quality and quantity of humus in raw waters and in drinking water, *Science of the Total environment*, **62**, 75-84.

Voss, R., Rapsomstiotis, A., (1985) An improved solvent-extraction based procedure for the gas chromatographic analysis of resin and fatty acids in pulp Mill effluents, *J. Chromatog.* **346**, 205-214.