

# High-molecular-weight effluent materials from modern ECF and TCF bleaching

Olof B. Dahlman, Anders K. Reimann, Lars M. Stromberg, and Roland E. Mörck

**ABSTRACT:** *The authors characterized chemical structure and properties of high-molecular-weight effluent materials (HMWM) from ECF and TCF bleaching of softwood and hardwood kraft pulps. Hardwood-derived HMWM were mainly nonaromatic, whereas aromatic lignin structures composed the softwood-derived HMWM. High carbohydrate levels occurred in HMWM from hardwood kraft mills with TCF bleaching using hydrogen peroxide. In their chlorine content and hydrophilic and polyelectrolytic characteristics, the investigated HMWM resembled aquatic humic substances.*

**KEYWORDS:** *Alkaline pulps, bibliographies, bleaching, bleaching effluents, chemical properties, chemical pulps, chemical treatment, chlorine free bleaching, dissolved solids, effluents, hardwood pulps, kraft pulps, molecular structure, molecular weight, organic materials, properties, pulps, softwood pulps, solids content, solutes, spent liquors, weight.*

The high-molecular-weight fraction of the organic material in effluents from modern bleached kraft mills contains a substantial portion of the total COD. In effluents from mills with essentially chlorine-free (ECF) bleaching, the high-molecular-weight materials (HMWM) also carry some small amounts of adsorbable organic halogens (AOX) found in such effluents.

After aerobic secondary effluent treatment, a dominant part of the

residual AOX in ECF effluents incorporates into organic material of high-molecular-weight (1). This agrees with the observation that secondary effluent treatment has less effect on HMWM than on low molecular weight compounds (1–4).

Our laboratory is currently investigating the nature of HMWM in biologically untreated and treated effluents from modern kraft pulp bleaching technologies. This paper reports a comprehensive character-

ization of HMWM in whole mill effluents and bleach plant effluents originating from Swedish kraft mills. The mills produced ECF bleached and totally chlorine free (TCF) bleached softwood and hardwood kraft pulps.

## Experimental

### Samples

The HMWM had molecular weights over 1000. Ultrafiltration (UF) isolated HMWM from ten bleached kraft mill effluents (BKME). The effluents came from five Swedish kraft mills using conventional or modified cooking, oxygen delignification, and ECF or TCF bleaching (Table I). Five of the effluents originated from three mills using chlorine dioxide based ECF bleaching. The other five effluents were from two mills with hydrogen peroxide based TCF bleaching.

ECF-1-SW-Bp (48-h composite sample) and ECF-2-HW-Bp (grab sample) were bleach plant effluents from mills using conventionally cooked, oxygen delignified, and ECF bleached softwood and hardwood kraft pulps, respectively. The hardwood derived effluents ECF-3-HW-D and ECF-4-HW-EP were grab samples after the first D-stage and after the EP-stage, respectively, at the same mill producing the bleach plant effluent ECF-2-HW-Bp. There was no bleach plant effluent sampling, however, simultaneously with the D-stage and EP-stage samples.

Dahlman, Reimann, and Mörck are research manager, research engineer, and senior research engineer, respectively, with Swedish Pulp and Paper Research Institute (STFI), Box 5604, S-11486 Stockholm, Sweden. Stromberg is now environmental coordinator with AssiDoman, S-10522 Stockholm, Sweden.

# Pulp Bleaching

## I. Cooking and bleaching processes

| <i>BKME sample</i>                   | <i>Pulp type</i>  | <i>Cooking process</i>          | <i>Bleaching process</i> |
|--------------------------------------|-------------------|---------------------------------|--------------------------|
| ECF-1-SW-Bp<br>Bleach plant effluent | Softwood<br>kraft | Conventional                    | OD(EOP)DED               |
| ECF-2-HW-Bp<br>Bleach plant effluent | Hardwood<br>kraft | Conventional                    | OD(EP)DED                |
| ECF-3-HW-D<br>D-stage effluent       | Hardwood<br>kraft | Conventional                    | OD(EP)DED                |
| ECF-4-HW-EP<br>EP-stage effluent     | Hardwood<br>kraft | Conventional                    | OD(EP)DED                |
| ECF-5-SW-Wh<br>Whole mill effluent   | Softwood<br>kraft | Mod. cooking<br>("Super Batch") | OD(EO)D(EP)D             |
| TCF-1-SW-Wh<br>Whole mill effluent   | Softwood<br>kraft | Mod. cooking<br>("Super Batch") | OQP                      |
| TCF-2-SW-P<br>P-stage effluent       | Softwood<br>kraft | Mod. cooking<br>("Super Batch") | OQP                      |
| TCF-3-HW-Wh<br>Whole mill effluent   | Hardwood<br>kraft | Conventional                    | OQP                      |
| TCF-4-HW-Bp<br>Bleach plant effluent | Hardwood<br>kraft | Conventional                    | OQP                      |
| TCF-5-HW-P<br>P-stage effluent       | Hardwood<br>kraft | Conventional                    | OQP                      |

## II. Process data during effluent sampling

|                                                                                                     | <i>ECF-1-SW-Bp</i> | <i>ECF-2-HW-Bp</i> | <i>ECF-3-HW-D</i> | <i>ECF-4-HW-EP</i> | <i>ECF-5-SW-Wh</i> | <i>TCF-1-SW-Wh</i> | <i>TCF-2-SW-P</i> | <i>TCF-3-HW-Wh</i> | <i>TCF-4-HW-Bp</i> | <i>TCF-5-HW-P</i> |
|-----------------------------------------------------------------------------------------------------|--------------------|--------------------|-------------------|--------------------|--------------------|--------------------|-------------------|--------------------|--------------------|-------------------|
| Kappa number after O-stage                                                                          | 17                 | 12                 | 12                | 12                 | 8.5                | 10                 | 10                | 12                 | 12                 | 12                |
| Total charge of ClO <sub>2</sub> , kg a. Cl ptp                                                     | 56                 | 50                 | 27*               | 27*                | 30                 | -                  | -                 | -                  | -                  | -                 |
| Oxygen charge in E-stages, kg ptp                                                                   | 3                  | -                  | -                 | -                  | 5                  | -                  | -                 | -                  | -                  | -                 |
| Total charge of H <sub>2</sub> O <sub>2</sub> , kg ptp                                              | 3                  | 2.5                | -                 | 2.5                | 2.2                | 36                 | 36                | 35                 | 35                 | 35                |
| Brightness, bleached pulp, % ISO                                                                    | 90.3               | n.d.               | 69                | n.d.               | 89.4               | 75                 | n.d.              | 82                 | n.d.               | n.d.              |
| * Charge of chlorine dioxide in the first D-stage<br>n.d. = not determined<br>ptp = per ton of pulp |                    |                    |                   |                    |                    |                    |                   |                    |                    |                   |

The whole mill effluent ECF-5-SW-Wh was a 6-h composite sample from an integrated softwood kraft mill equipped with extended delignification in the cooking stage ("Super Batch"), oxygen delignification, and ECF bleaching. Because of the extended delignification in the cooking stage, the pulp entering the bleach plant was kappa no. 8.5. **Table II** shows that this low kappa number made it possible to reduce the charge

of chlorine dioxide in the bleaching process.

The effluents TCF-1-SW-Wh (6-h composite sample from whole mill effluent) and TCF-2-SW-P (grab sample from P-stage effluent) were from different times at a mill with production of TCF bleached softwood kraft pulp. This mill also used extended delignification to low kappa number combined with oxygen

delignification. After O-stage, kappa no. was 10.

The effluents TCF-3-HW-Wh (11-h composite sample from whole mill effluent), TCF-4-HW-Bp (grab sample from bleach plant effluent), and TCF-5-HW-P (grab sample from P-stage effluent) came from a mill using conventionally cooked and TCF bleached hardwood kraft pulp. The effluents represent different sampling times.

### III. General effluent parameters and results from UF

| Effluent    | COD,<br>kg ptp | COD > 1000,<br>% | AOX,<br>kg ptp | AOX > 1000,<br>% | HMWM |
|-------------|----------------|------------------|----------------|------------------|------|
| ECF-1-SW-Bp | 31             | 45               | 0.7            | 40               | 10.6 |
| ECF-2-HW-Bp | 25             | 40               | 0.5            | 35               | 8.0  |
| ECF-3-HW-D  | 11             | 31               | 0.3            | 18               | 2.5  |
| ECF-4-HW-EP | 15             | 61               | 0.1            | 74               | 5.5  |
| ECF-5-SW-Wh | 57             | 43               | 0.2            | 47               | 12.3 |
| TCF-1-SW-Wh | 41             | 33               | 0.01           | n.d.             | 9.6  |
| TCF-2-SW-P  | 27             | 56               | n.d.           | n.d.             | 9.8  |
| TCF-3-HW-Wh | 30             | 31               | 0.01           | n.d.             | 7.7  |
| TCF-4-HW-Bp | 16             | 41               | 0.002          | n.d.             | 6.2  |
| TCF-5-HW-P  | 11             | 39               | n.d.           | n.d.             | 3.7  |

### IV. Elemental composition, chlorine content, and C/Cl ratio

| Sample      | Elemental composition                                                                                      | Cl, % | C/Cl  |
|-------------|------------------------------------------------------------------------------------------------------------|-------|-------|
| ECF-1-SW-Bp | C <sub>100</sub> H <sub>129</sub> N <sub>0.3</sub> O <sub>62</sub> S <sub>1.6</sub> Cl <sub>1.1</sub>      | 1.4   | 90    |
| ECF-2-HW-Bp | C <sub>100</sub> H <sub>148</sub> N <sub>0.4</sub> O <sub>70</sub> S <sub>2.9</sub> Cl <sub>1.2</sub>      | 1.5   | 83    |
| ECF-3-HW-D  | C <sub>100</sub> H <sub>147</sub> N <sub>0.9</sub> O <sub>66</sub> S <sub>1.4</sub> Cl <sub>1.8</sub>      | 2.3   | 56    |
| ECF-4-HW-EP | C <sub>100</sub> H <sub>152</sub> N <sub>0.4</sub> O <sub>63</sub> S <sub>1.0</sub> Cl <sub>0.84</sub>     | 1.1   | 119   |
| ECF-5-SW-Wh | C <sub>100</sub> H <sub>125</sub> N <sub>1.2</sub> O <sub>68</sub> S <sub>2.3</sub> Cl <sub>0.38</sub>     | 0.51  | 260   |
| TCF-1-SW-Wh | C <sub>100</sub> H <sub>131</sub> N <sub>0.6</sub> O <sub>77</sub> S <sub>1.9</sub> Cl <sub>&lt;0.08</sub> | <0.1  | >1200 |
| TCF-2-SW-P  | C <sub>100</sub> H <sub>115</sub> N <sub>0.4</sub> O <sub>61</sub> S <sub>0.6</sub> Cl <sub>0.081</sub>    | 0.11  | 1200  |
| TCF-3-HW-Wh | C <sub>100</sub> H <sub>145</sub> N <sub>1.1</sub> O <sub>89</sub> S <sub>2.3</sub> Cl <sub>0.069</sub>    | 0.08  | 1400  |
| TCF-4-HW-Bp | C <sub>100</sub> H <sub>173</sub> N <sub>1.0</sub> O <sub>84</sub> S <sub>1.3</sub> Cl <sub>0.17</sub>     | 0.19  | 590   |
| TCF-5-HW-P  | C <sub>100</sub> H <sub>156</sub> N <sub>0.3</sub> O <sub>80</sub> S <sub>0.9</sub> Cl <sub>0.17</sub>     | 0.20  | 590   |

## Methods

**Ultrafiltration.** UF of the studied effluents used a pH value of 7 with commercially available, tangential flow equipment. The membrane was a commercially available, low absorbing polysulfone having a nominal cut-off at 1000. All effluents underwent prefiltering before UF using a filter with a pore size of 1.2  $\mu$ m.

The UF began with an effluent volume of 10–15 L and ended with a

concentrate volume of 0.5 L. The UF concentrates then underwent sequential batch diafiltration (5) using 5 x 1.0 L of pure water. This removed inorganic salts and organic compounds of low molecular weight. The purified UF concentrates (HMWM) next underwent freeze drying.

**Elemental analysis, functional groups, and carbohydrates.** A Swedish testing laboratory did the elemen-

tal analyses, and a commercially available atomic absorption spectrometer determined the metal contents. A German testing laboratory determined the methoxyl group contents. Conductometric titration on ion exchanged samples provided the content of carboxylic acid groups. Selective aminolysis of ion exchanged and acetylated samples using a method for selective aminolysis of lignins (6) determined the phenolic hydroxyl groups. The method of Theander and Westerlund (7) provided the carbohydrate content.

**Chemical degradation.** Permanganate oxidation using the procedure of Gellerstedt and Gustafsson (8) provided oxidative degradation. Thioacidolysis used the method developed by Lapierre *et al.* (9).

**<sup>13</sup>C NMR spectroscopy.** <sup>13</sup>C NMR spectra of ion exchanged samples were recorded in DMSO-d<sub>6</sub> solution. Sample concentration was 300 mg/mL, temperature was 50°C, and pulses were 30° at 75.47 MHz using a commercial nuclear magnetic resonance (NMR) spectrometer. Pulse repetition time was 1.0 s.

|             | Carbo-<br>hydrates, % | Relative distribution, % |        |         |           |         |
|-------------|-----------------------|--------------------------|--------|---------|-----------|---------|
|             |                       | Arabinose                | Xylose | Mannose | Galactose | Glucose |
| ECF-1-SW-Bp | 8.9                   | 7                        | 14     | 3       | 45        | 31      |
| ECF-2-HW-Bp | 17.6                  | 3                        | 81     | -       | 7         | 9       |
| ECF-3-HW-D  | 13.0                  | 5                        | 61     | -       | 19        | 15      |
| ECF-4-HW-EP | 18.3                  | 3                        | 82     | 1       | 4         | 10      |
| ECF-5-SW-Wh | 3.5                   | 11                       | 26     | 11      | 29        | 23      |
| TCF-1-SW-Wh | 18.0                  | 7                        | 61     | 6       | 12        | 14      |
| TCF-2-SW-P  | 13.5                  | 7                        | 48     | 7       | 18        | 20      |
| TCF-3-HW-Wh | 40.8                  | 2                        | 93     | -       | 3         | 2       |
| TCF-4-HW-Bp | 47.7                  | 1                        | 95     | -       | 2         | 2       |
| TCF-5-HW-P  | 37.5                  | 2                        | 91     | -       | 4         | 3       |

## Results and discussion

### Isolation of HMWM

UF separated the organic material in each effluent into two fractions. By definition, the HMWM, i.e., the UF-concentrate, was the fraction of the organic material in each effluent which upon UF followed by sequential batch diafiltration (5), could not penetrate the UF membrane used. It therefore remained in the concentrate.

**Table III** shows the fractionation results. The HMWM carried 31–45% of the total effluent load of COD in the bleach plant and whole mill effluents investigated. This indicates that the HMWM in these effluents constituted a substantial but not dominant part of the total organic effluent material.

The results in **Table III** further show that the HMWM carried comparatively small parts of the total COD and AOX loads in the D-stage effluent (ECF-3-HW-D) from ECF bleaching of hardwood kraft pulp. The HMWM in the following EP-stage carried major parts of the total loads of COD and AOX. This

indicates that the organic material dissolved in the first D-stage had low molecular weight. A material of higher molecular weight dissolved from the pulp in the succeeding EP-stage (effluent ECF-4-HW-EP). The larger molecules dissolved in the EP-stage probably require ionization of their dissociable groups before they can be extracted from the pulp.

### Elemental composition

**Table IV** shows the elemental composition of the freeze-dried HMWM. The samples originating from mills with ECF bleaching exhibited chlorine contents of 0.5–2.3% by weight. It is not surprising that the HMWM sample originating from the combination of modified kraft cooking, oxygen delignification, and ECF bleaching of softwood kraft pulp (ECF-5-SW-Wh) showed the lowest value of 0.5%. Note that the chlorine content in this sample was only slightly higher than the chlorine contents found in some chlorinated humic materials of natural origin (10, 11).

As one might expect, the D-stage HMWM sample ECF-3-HW-D

showed a higher chlorine content than the HMWM sample from the succeeding EP-stage (ECF-4-HW-EP). The C/Cl ratios found in these two HMWM samples agreed well with previously published values for HMWM from the D- and E-stages obtained upon laboratory bleaching of softwood kraft pulp using the sequence DE (12, 13).

The TCF derived HMWM studied also contained some chlorine, although the quantities were only 0.08–0.2%. Such levels are comparable to the chlorine contents found in naturally occurring humic materials (10, 11).

### Carbohydrate content

The results in **Table V** show that all HMWM studied contained carbohydrates. Note that all effluents studied were prefiltered before UF using a filter with a pore size of 1.2 µm. This removed fiber residues and particles before UF. The carbohydrates found as constituents of the HMWM investigated must therefore have been oligosaccharides, polysaccharides, or both present in the effluents either in dissolved or colloidal form.

# VI. Contents of carboxylic acid groups, methoxyl groups, and phenolic hydroxyl groups

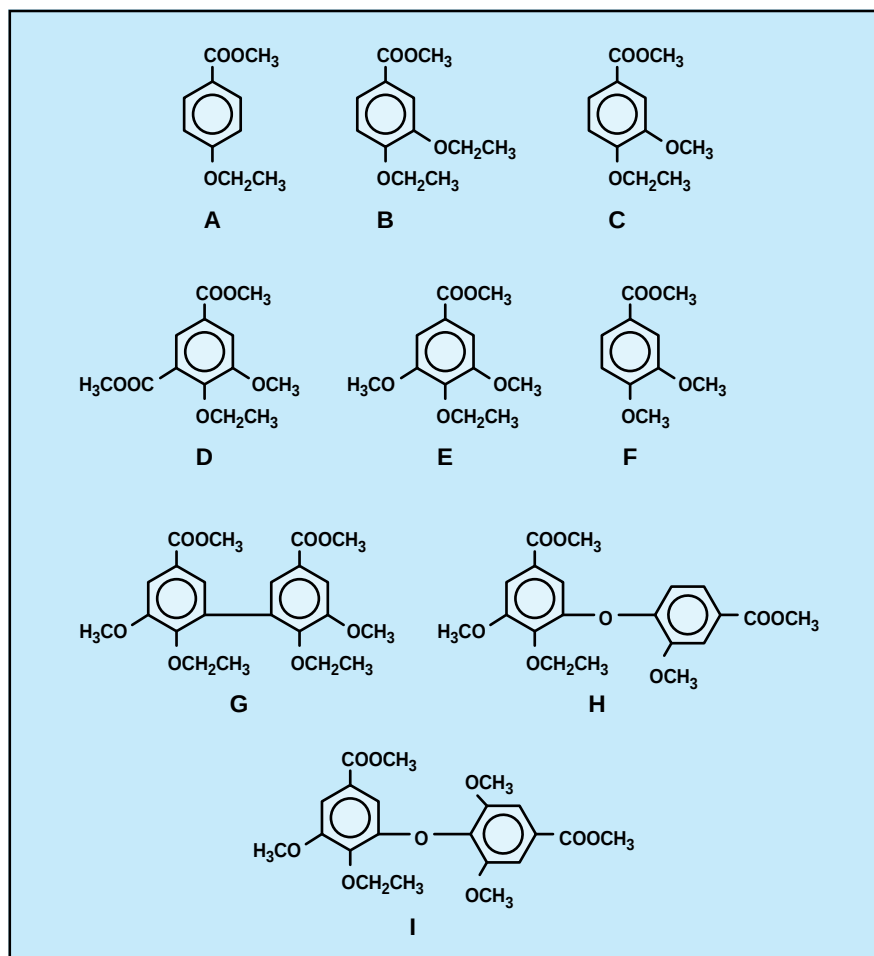
|                         | Carboxyl groups, mmol/g | Methoxyl groups, mmol/g | Phenolic hydroxyl groups, mmol/g |
|-------------------------|-------------------------|-------------------------|----------------------------------|
| ECF-1-SW-Bp             | 2.9                     | 1.7                     | 0.6                              |
| ECF-2-HW-Bp             | 3.3                     | 0.7                     | 0.6                              |
| ECF-3-HW-D              | 3.1                     | 0.7                     | 0.8                              |
| ECF-4-HW-EP             | 2.8                     | 0.7                     | 0.6                              |
| ECF-5-SW-Wh             | 2.4                     | 1.2                     | 1.8                              |
| TCF-1-SW-Wh             | 3.6                     | 1.2                     | 0.8                              |
| TCF-2-SW-P              | 3.4                     | 1.8                     | 1.1                              |
| TCF-3-HW-Wh             | 2.8                     | 0.7                     | 0.6                              |
| TCF-4-HW-Bp             | 2.8                     | 0.5                     | n.d.                             |
| TCF-5-HW-P              | 2.7                     | 0.6                     | n.d.                             |
| Kraft lignin (hardwood) | 0.4*                    | 6-6.5                   | 4                                |
| Kraft lignin (softwood) | 0.8                     | 4-4.5                   | 4                                |

\*Birch kraft lignin from STFI unpublished results

The hardwood derived HMWM samples from mills with hydrogen peroxide based TCF bleaching contained more carbohydrates (mainly xylan) than comparable hardwood derived samples from mills with ECF bleaching (Table V). Similar differences in carbohydrate content also exist between TCF related and ECF related HMWM samples from softwood effluents. A possible explanation to these differences is that the process conditions in the P-stage (long retention time under alkaline conditions) may favor dissolution of xylan from the pulp.

Table V also reveals that the HMWM originating from production of hardwood kraft pulps contained more carbohydrates (mainly xylan) than the corresponding HMWM samples from production of softwood kraft pulp.

## 1. Types of aromatic degradation products (derivatized) obtained upon permanganate oxidation of HMWM



## Functional groups

Table VI shows the contents of methoxyl groups, phenolic hydroxyl groups, and carboxylic acid groups in the HMWM studied. Literature values for the contents of these functional groups in softwood and hardwood kraft lignins are also in the table for reference (14–17). Note that the contents of carboxylic acid groups and methoxyl groups in the HMWM (Table VI) do not contain a correction for carbohydrate content. The values for phenolic hydroxyls do have this correction.

All HMWM samples studied in the present investigation showed high levels of carboxylic acid groups compared to kraft lignins. This is normal considering the reactions taking place in the oxidative bleaching stages (18–21) that transform the residual lignin in the pulp into oxidized structures rich in carboxylic acid groups. The introduction of carboxylic acid groups is favorable for the bleaching result. These ionizable groups help the dissolution of the residual lignin from the pulp.

The contents of carboxylic acid groups found in the HMWM samples from ECF bleaching (Table VI) were

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lower than in a previous investigation (22) studying HMWM originating from chlorine based bleaching. This contradicts results from studies on HMWM in liquors from laboratory bleaching of softwood kraft pulps previously published by Osterberg and Lindstrom (12, 13).

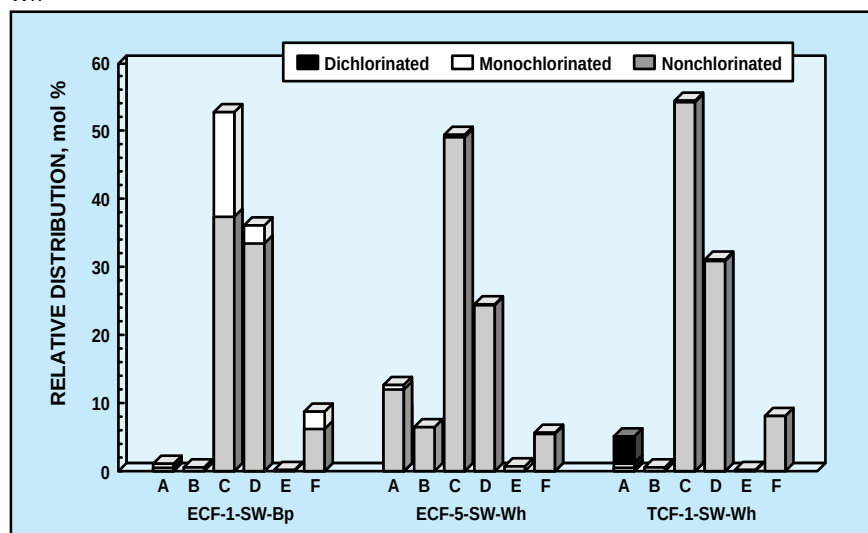
All HMWM samples studied including those originating from TCF bleaching showed lower contents of methoxyl groups and phenolic hydroxyl groups than kraft lignins (Table VI). The methoxyl group content of the softwood derived bleach plant HMWM samples ECF-1-SW-Bp and TCF-2-SW-P, after correction for carbohydrates, therefore amounted to approximately 40–45% of the methoxyl group content normally found in softwood kraft lignin. A similar comparison between the methoxyl group contents in the hardwood derived bleach plant HMWM and hardwood kraft lignin showed that these HMWM samples contained only about 15% of the methoxyls normally found in hardwood kraft lignin. These comparisons strongly indicate that the hardwood derived HMWM studied were more degraded than the softwood derived HMWM.

The contents of phenolic hydroxyl groups were low in all samples studied. In the HMWM originating from bleach plant effluents, they comprised approximately 15–25% of the values normally found in kraft lignins.

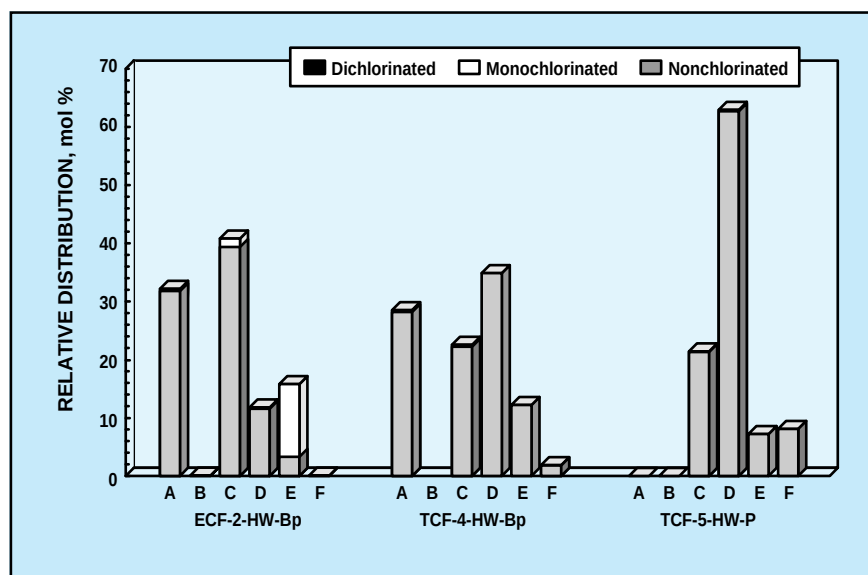
An interesting observation from the data in Table VI is that the softwood derived bleach plant HMWM studied (ECF-1-SW-Bp and TCF-2-SW-P) showed a significantly higher molar content of methoxyl groups than phenolic hydroxyls. This indicates the presence of ether linked guaiacyl units in the softwood HMWM samples.

Comparisons between HMWM and humic substances are of environmental interest. Both humic substances and HMWM contain high levels of carboxylic acid groups. The contents of carboxylic acids found in

2. Relative distribution of degradation products A–F of Fig. 1 obtained upon permanganate oxidation of the softwood-derived HMWM ECF-1-SW-Bp, ECF-5-SW-Wh, and TCF-1-SW-Wh



3. Relative distribution of degradation products A–F of Fig. 1 obtained upon permanganate oxidation of the hardwood-derived HMWM ECF-2-HW-Bp, TCF-4-HW-Bp, and TCF-5-HW-P

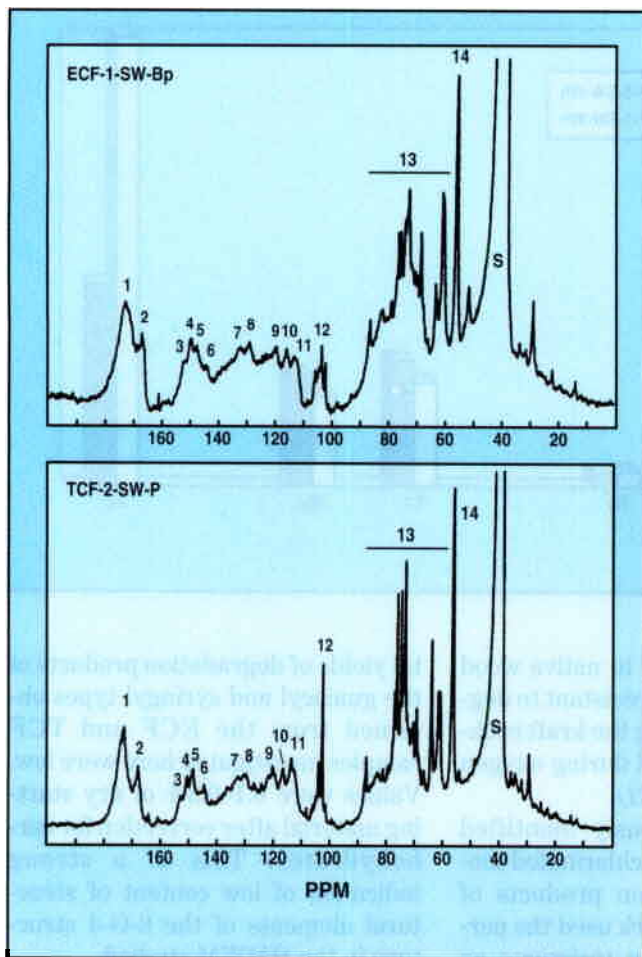


the present investigation were lower than those found in humic substances (4.5–6.5 mmol/g) isolated from Finnish lake waters (23, 24) and American rivers (25). The content of phenolic hydroxyl groups in the HMWM studied here were also lower than the values (1.5–2 mmol/g) reported for humic substances from Finnish lakes (23, 24).

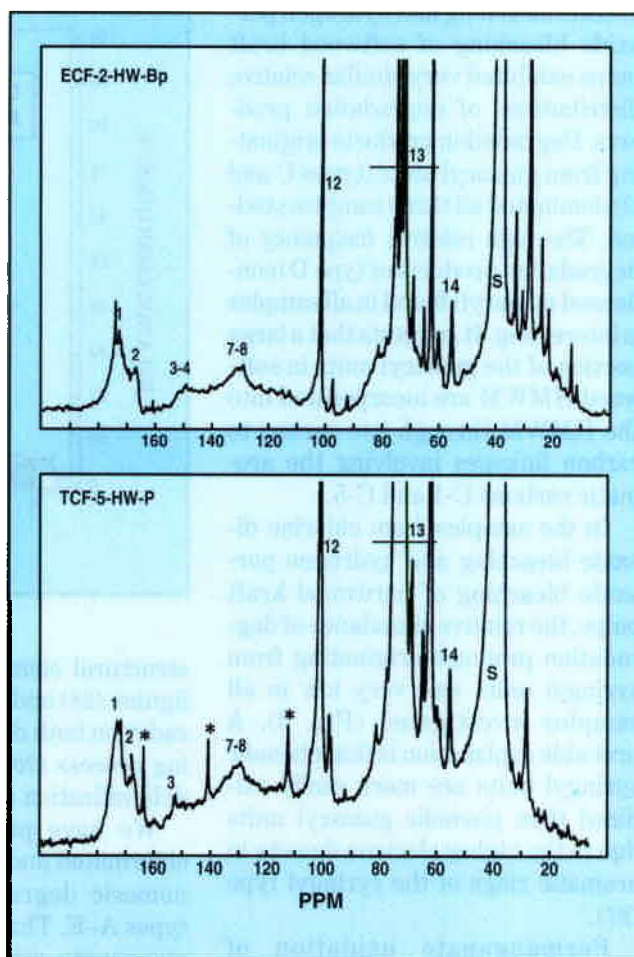
## Chemical degradation

**Permanganate oxidation.** Permanganate oxidation provides information about the composition of the residual phenolic structural elements in lignin derived, high-molecular-weight BKME materials (1, 12, 13, 22). **Figure 1** shows the major types of monomeric lignin related degradation products obtained in the present study. The degradation products A–F originate from residual 4-hydroxyphenyl (A), 3,4-

4.  $^{13}\text{C}$  NMR spectra of the softwood-derived HMWM ECF-1-SW-Bp and TCF-2-SW-P (S = solvent)



5.  $^{13}\text{C}$  NMR spectra of the hardwood-derived HMWM ECF-2-HW-Bp and TCF-5-HW-P (S = solvent)



dihydroxyphenyl (B), guaiacyl (C), "condensed" guaiacyl (D), and syringyl units (E) present as structural elements in the HMWM. Degradation products of the veratryl type (F) were also present. It is not certain, however, whether the veratryl degradation products originate from lignin.

Besides the monomeric degradation products A-F, three lignin derived dimeric degradation products (G-I) originating from diphenyl (G) and diphenyl ether units (H-I) were also found upon analysis of the degraded samples (Fig. 1).

The work identified all six types of monomeric degradation products shown in Fig. 1 in both their nonchlorinated and chlorinated forms. The chlorinated forms were mostly present only in very small

quantities. No chlorinated dimeric degradation products were found in any of the degraded samples investigated.

Compared to literature values from permanganate oxidation of nonoxidized lignins (8, 26), the total yield of degradation products obtained from the ECF and TCF samples investigated here were quite low. Values were 0.2–1.9% of dry starting material, after correction for carbohydrates. This is a clear indication of low content of phenolic structural elements in the ECF and TCF materials studied.

Figure 2 shows the relative distribution of the quantities of the degradation products obtained from the softwood HMWM. Figure 3 shows the results from degradation of the hardwood HMWM. The results in-

dicate that the major part of the residual phenolic structural elements in HMWM from mills with ECF bleaching is nonchlorinated, although a minor part is monochlorinated. The low degree of chlorination in the phenolic structural elements is especially evident for the HMWM sample ECF-5-SW-Wh. An important conclusion from these results is that there is no reason to fear that degradation of HMWM from ECF bleaching in receiving waters should lead to the formation of highly chlorinated monomeric phenolic compounds.

Note that trace amounts of chlorinated degradation products were also present in the degraded TCF samples. The quantities were too small to be visible in Figs. 2–3, however.

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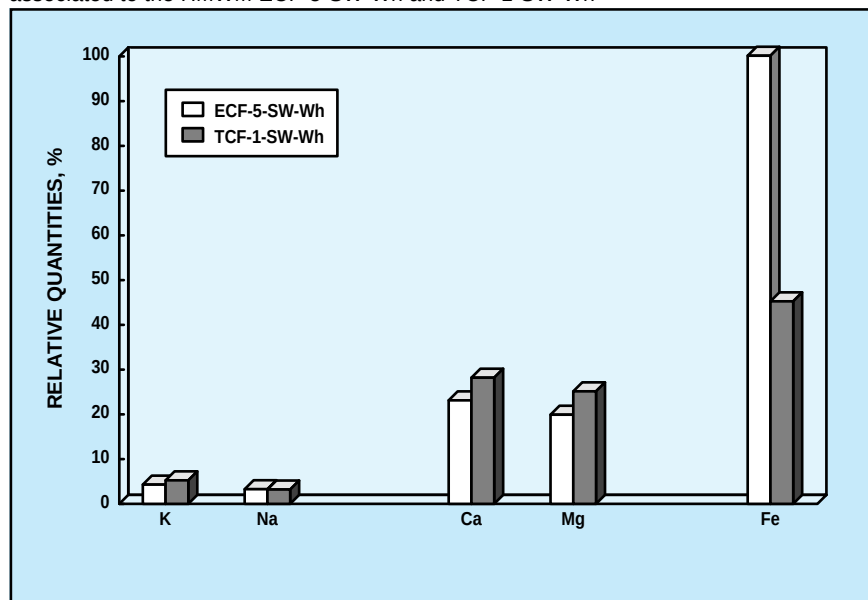
As Fig. 2 indicates, the HMWM samples originating from chlorine dioxide bleaching and hydrogen peroxide bleaching of softwood kraft pulps exhibited very similar relative distributions of degradation products. Degradation products originating from guaiacyl units (types C and D) dominated all three samples studied. The high relative frequency of degradation products of type D (condensed guaiacyl) found in all samples is interesting. It suggests that a large portion of the guaiacyl units in softwood HMWM are incorporated into the HMWM through two carbon to carbon linkages involving the aromatic carbons C-1 and C-5.

In the samples from chlorine dioxide bleaching and hydrogen peroxide bleaching of hardwood kraft pulps, the relative abundance of degradation products originating from syringyl units was very low in all samples investigated (Fig. 3). A probable explanation is that phenolic syringyl units are more easily oxidized than phenolic guaiacyl units due to the higher electron density in aromatic rings of the syringyl type (27).

Permanganate oxidation of HMWM samples originating from hydrogen peroxide bleaching of hardwood kraft pulp (TCF-4-HW-Bp and TCF-5-HW-P) revealed that condensed guaiacyl units (type D) occurred more frequently than uncondensed guaiacyl units in these samples (Fig. 3). There was no such relationship between condensed and uncondensed guaiacyl units for the softwood HMWM sample TCF-1-SW-Wh (Fig. 2), however. This is difficult to explain.

The dimeric degradation products identified in Fig. 1 that originated from biphenyl (G) and biphenyl ether (H and I) structures constituted about 1–7% of the total degradation products obtained from the bleach plant effluent HMWM studied and about 9–14% of the degradation products obtained from the whole mill effluent HMWM. Biphenyl and biphenyl ether units are common

6. Relative quantities as a percentage of the total in the effluent of K, Na, Ca, Mg and Fe associated to the HMWM ECF-5-SW-Wh and TCF-1-SW-Wh



structural elements in native wood lignins (28) and are resistant to degradation both during the kraft cooking process (29) and during oxygen delignification (30, 31).

We have previously identified chlorinated and nonchlorinated monomeric degradation products of types A–E. That work used the permanganate oxidation technique on naturally occurring humic materials (fulvic acids) isolated from industrially unpolluted surface waters and ground waters (11, 32). A comparison of the results obtained upon permanganate oxidation of fulvic acids with the results from the present investigation show that HMWM from both chlorine dioxide bleaching and hydrogen peroxide bleaching of kraft pulp contain the same types of phenolic structural elements as those found in naturally occurring humic materials.

**Thioacidolysis.** To determine whether nonphenolic alkyl-aryl ether structures such as  $\beta$ -O-4 structures were present as structural elements in the HMWM, the samples studied underwent thioacidolysis according to the method developed by Lapierre *et al.* (9). Compared to literature values from thioacidolysis of wood lignins and kraft lignins (33), the to-

tal yields of degradation products of the guaiacyl and syringyl types obtained from the ECF and TCF samples investigated here were low. Values were 0.1–0.3% of dry starting material after correction for carbohydrates. This is a strong indication of low content of structural elements of the  $\beta$ -O-4 structure in the HMWM studied.

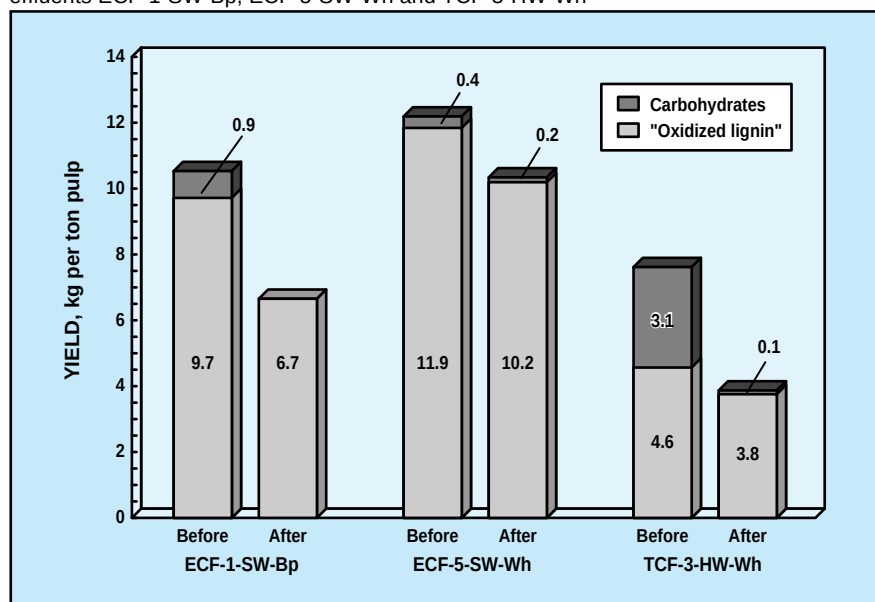
The combined results from permanganate oxidation and thioacidolysis show low content of phenolic structural elements and low content of nonphenolic structures of the  $\beta$ -O-4 type in the HMWM samples. We cannot exclude the presence of other types of nonphenolic lignin structures such as diaryl ethers, however, from these results. Diaryl ether structures are common in residual lignins isolated from oxygen delignified kraft pulps (30, 31).

### <sup>13</sup>CNMR spectroscopy

**Figures 4 and 5** show <sup>13</sup>C NMR spectra of selected softwood derived (Fig. 4) and hardwood derived (Fig. 5) HMWM (ion exchanged samples) recorded in a nonquantitative mode from DMSO-d<sub>6</sub> solutions.

All four spectra in the figures show two broad and intense signals

7. Yield of HMWM before and after secondary effluent treatment obtained upon UF of the effluents ECF-1-SW-Bp, ECF-5-SW-Wh and TCF-3-HW-Wh



assigned to carboxylic acid carbons (signals 1 and 2). The intensities of these signals confirm that the HMWM studied are rich in carboxylic acid groups. The chemical shifts of these two signals indicate that signal 1 (172–173 ppm) mainly originates from carbon atoms in carboxylic acid groups bound to saturated aliphatic structures (34). Signal 2 (167–168 ppm) may represent carbon atoms in carboxylic acid groups conjugated to aromatic or olefinic structures (34).

The intensity of the signal clusters 12 and 13 (Figs. 4 and 5) confirmed the presence of carbohydrates in the HMWM studied. The three sharp signals at 163.7, 141.0, and 113.0 ppm, marked with asterisks in the spectrum of the HMWM sample TCF-5-HW-P (Fig. 5) originate from unsaturated uronic acid units (35) present as structural elements in the xylan after kraft pulping. The presence of these signals suggests that the unsaturated uronic acid units “survive” during hydrogen peroxide bleaching.

Figure 4 shows the  $^{13}\text{C}$  NMR spectra of the softwood derived HMWM samples ECF-1-SW-Bp and TCF-2-SW-P. It shows that the spectra of

these samples were quite similar especially in the region 110–200 ppm. In this region, signals from aromatic carbons, olefinic carbons, and carbonyl carbons appear. The pattern of signals in the aromatic region (110–160 ppm) of the spectra shown in Fig. 4 resembles the signal pattern normally found in spectra of nonoxidized softwood lignins (34, 36, 37). This indicates that HMWM in effluents from chlorine dioxide bleaching or hydrogen peroxide bleaching of oxygen delignified softwood kraft pulp retain their aromatic nature to a significant degree. The presence of the signals 9, 10, and 11 assigned to the unsubstituted C-6, C-5, and C-2 carbons, respectively in guaiacyl units and the presence of signals 3–8 assigned to the oxygen substituted C-3 and C-4 carbons (signals 3–6) and the C-substituted C-1 carbon (signals 7–8) in guaiacyl units indicate this. These assignments were based on the comprehensive  $^{13}\text{C}$  NMR studies on lignins and lignin model compounds previously published (34, 36, 38, 39).

The  $^{13}\text{C}$  NMR spectra of the samples ECF-1-SW-Bp and TCF-2-SW-P therefore strongly suggest that a substantial part of the guaiacyl

units in the residual lignin in softwood kraft pulp “survives” under the conditions used for chlorine dioxide bleaching and hydrogen peroxide bleaching. The low levels of phenolic hydroxyl groups and the low yield of degradation products obtained upon oxidative degradation may indicate that a major part of these guaiacyl units is etherified.

Figure 5 shows the  $^{13}\text{C}$  NMR spectra of the hardwood derived HMWM samples ECF-2-HW-Bp and TCF-5-HW-P. These spectra differ significantly from those of the softwood derived HMWM in Fig. 4. This is partly due to the high intensity of the carbohydrate signals 12 and 13 that reflects the higher content of carbohydrates in the hardwood derived HMWM samples.

The most interesting differences between the spectra of the softwood derived and hardwood derived HMWM are in the aromatic region (110–160 ppm), however. The signals assigned to guaiacyl carbons in the spectra of the softwood derived HMWM (Fig. 4) are virtually absent in the spectra of the hardwood derived HMWM in Fig. 5. Etherified syringyl units should, if present in significant quantities, produce two strong signals at 105 ppm and 153 ppm (C-2/C-6 and C-3/C-5 respectively). These signals are also absent or very weak in the spectra shown in Fig. 5. Instead, the dominating signal in this region of the spectra in Fig. 5 is the broad signal appearing at approximately 125–135 ppm assigned to olefinic carbons.

The  $^{13}\text{C}$  NMR spectra in Fig. 5 thus strongly indicate that aromatic lignin derived structures such as syringyl and guaiacyl units are not important structural elements in high-molecular-weight effluent materials from chlorine dioxide bleaching and hydrogen peroxide bleaching of oxygen delignified hardwood kraft pulps. Instead, the hardwood derived HMWM are composed mainly of nonaromatic structural elements. The reason for this is not completely clear. A part of the explanation may

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be that syringyls—common constituents of hardwood lignins—are more susceptible to oxidative cleavage in their phenolic form than other types of aromatic lignin structures. This is due to the greater electron density in the syringyl ring (27).

### Associated metals

A separate study assessed the ability of HMWM to attract various metal ions normally occurring in the effluents investigated. We studied this because the HMWM samples examined (also those originating from TCF bleaching) were heavily oxidized and exhibited high levels of carboxylic acid groups. It is therefore reasonable to expect that these HMWM under neutral or alkaline conditions can function as anionic polyelectrolytes able to attract metal ions.

We determined the contents of some common metal ions ( $K^+$ ,  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , and  $Fe^{3+}$ ) separately in the unfractionated neutralized effluents and in the HMWM isolated by UF. We compared the results from the separate determinations and then estimated the relative quantities of the metal ions associated to the HMWM in the neutralized effluents. **Figure 6** shows that only minor parts of the total content of the monovalent metal ions  $K^+$  and  $Na^+$  were associated to the HMWM. This is not unexpected, since these metal ions can only form comparatively weak electrostatic linkages to anionic positions in organic materials.

Somewhat larger parts of the total contents of the divalent ions  $Ca^{2+}$  and  $Mg^{2+}$  were associated with the HMWM (Fig. 6). These metal ions form comparatively weak complexes of an electrostatic nature with suitable positions in anionic organic materials.

The trivalent metal ion  $Fe^{3+}$  had a stronger association to the HMWM in the ECF effluent ECF-5-SW-Wh (Fig. 6). This is not surprising, since trivalent metal ions form strong chelate complexes with anionic organic materials. The portion of the total

$Fe^{3+}$ -ions associated to the HMWM in the TCF effluent TCF-1-SW-Wh was lower than in the corresponding ECF effluent ECF-5-SW-Wh, however. This is probably due to the presence of the complexing agent EDTA in the TCF effluent.

In agreement with previous studies (1, 22, 40), our work supports the view that high-molecular-weight BKME materials can attract metal ions—especially divalent and trivalent ions. In this respect, HMWM exhibit properties similar to aquatic humic materials that bind and transport metal ions (41–44).

### Effects of secondary effluent treatment

To assess the biodegradability of HMWM from ECF and TCF bleaching, HMWM underwent isolation by UF from three effluents (ECF-1-SW-Bp, ECF-5-SW-Wh and TCF-3-HW-Wh) subjected to secondary effluent treatment. The treated effluent samples were collected from the same mills at the same times as the corresponding untreated effluents. A comparison between the HMWM isolated from these untreated and treated BKME should therefore give relevant information concerning the biodegradability of the HMWM studied.

The treated BKME ECF-1-SW-Bp and TCF-3-HW-Wh underwent treatment in an activated sludge plant (pilot plant with anoxic prezone and hydraulic retention time of approximately 12–16 h). The treated effluent ECF-5-SW-Wh had undergone treatment in an aerated lagoon with anoxic zones (hydraulic retention time approximately four days).

After UF at nominal cut-off of 1000, the organic material found in the concentrates, i.e., the HMWM, represented about 55–65% of the total COD load in the treated BKME. **Figure 7** shows the yields of freeze dried HMWM obtained upon UF of the effluents ECF-1-SW-Bp, ECF-5-SW-Wh, and TCF-3-HW-Wh before and after secondary effluent treatment. As the figure shows, sec-

ondary effluent treatment strongly affected the carbohydrate constituent of the HMWM. Other constituents of the HMWM denoted in the figure as “oxidized lignin” were less affected.

Permanganate oxidation of the HMWM samples isolated after aerobic effluent treatment showed that degradation products of the guaiacyl and syringyl types were less abundant than in the untreated samples. Instead, degradation products of the “condensed” guaiacyl type were more abundant in the treated samples. This result indicates that the bacteria in aerobic treatment plants may degrade guaiacyl and syringyl end groups in oxidized and dissolved lignin residues, although the degradation of the oxidized lignin material appears to be slow.

### Conclusion

The conclusions from this study will focus on three aspects:

- Properties of the investigated HMWM that are important from an environmental concept
- Similarities and differences between HMWM from hardwood and softwood derived BKME
- Similarities and differences between HMWM from ECF bleaching and TCF bleaching.

The results from the present investigation show that HMWM from kraft mills using ECF or TCF bleaching are primarily nonphenolic in nature. They comprise strongly oxidized, hydrophilic materials rich in carboxylic acid groups. Furthermore, the chlorine content in the HMWM is very low in comparison with corresponding materials from chlorine bleaching previously studied (22). The chlorine content in some ECF derived samples is only slightly higher than in some chlorinated humic materials of natural origin. The content of chlorine in the TCF derived samples is fully comparable to that in naturally occurring humic

materials. In several respects such as the types of remaining phenolic structural elements and the ability to act as an anionic polyelectrolyte, the investigated HMWM resemble aquatic humic substances. Although the degradation of the HMWM appears rather slow under aerobic conditions, the data presented here make it reasonable to assume that the fate of these HMWM will be similar to that of aquatic humic substances of natural origin.

Several noteworthy similarities and differences occurred with the HMWM originating from hardwood and softwood kraft pulps. The results from determination of the content of methoxyl groups, chemical degradation (permanganate oxidation and thioacidolysis), and  $^{13}\text{C}$  NMR spectroscopy show that the hardwood derived HMWM are mainly nonaromatic in nature. In contrast, the  $^{13}\text{C}$  NMR spectra of the softwood HMWM strongly suggest that a substantial part of the guaiacyl units in the residual lignin in softwood kraft pulp "survives" under the conditions used for ECF bleaching and hydrogen peroxide based TCF bleaching. The low levels of phenolic hydroxyl groups and the low yield of degradation products obtained upon permanganate oxidation and thioacidolysis suggest that a large part of these guaiacyl units incorporate into the HMWM as etherified structural elements of the diaryl ether or phenylcoumaran types.

The results from this study show that the HMWM originating from mills with hydrogen peroxide-based TCF bleaching generally contain more carbohydrates than comparable samples from mills with chlorine dioxide-based ECF bleaching. As expected, the chlorine content of the HMWM originating from TCF bleaching are lower than the chlorine content found in the HMWM originating from ECF bleaching. The results of this investigation indicate that the HMWM from TCF bleaching and the corresponding

materials from ECF bleaching exhibit great similarities in chemical structure and properties, however. 

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