Metal Profiling of Southeastern US SW and HW Wood Furnish

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ABSTRACT: A series of SW and HW wood chips, acquired from kraft pulping operations in the southeastern US, were analyzed for metals content by Inductively Coupled Plasma (ICP). Non-process element (NPE) analysis of the acid hydrolyzed woodchip samples suggested that the relative concentration of metals was Ca> K> Mg>Mn> (Na, Ba) > Fe. Distinct differences were noted between SW and HW wood chip samples, with the latter samples having higher absolute values of NPEs. ICP analysis of bark samples indicated this material had significantly higher values of Ca, K, and Mg than the corresponding wood chips.

INTRODUCTION

Reduced mill effluent operations are becoming a viable technological approach to minimizing the impact of pulp and paper operations on the surrounding environment. As mill system closure programs are implemented, various new operational challenges develop, including an accumulation of inorganic non-process elements (NPEs) originating from the wood. Non-process elements commonly include aluminum, barium, calcium, sodium, potassium, magnesium, manganese, iron, and silicon.[1, 2] Mill control of NPEs requires several control strategies; for example, potassium is very water soluble and difficult to purge from aqueous process streams although it can lead to plugging in a recovery boiler.[3] Other elements such as calcium and barium have distinct solubility profiles that can lead to scaling in the bleach plant or recovery cycle.[4] Finally, elements such as iron and manganese can detrimentally impact the performance of oxygen-based bleaching agents.[5,6] Management of mill NPEs is critically dependent on the use of computational modeling programs that predict how they distribute themselves in various process streams.[7] Current research efforts are beginning to establish the fundamental principals[8,9] and modeling capabilities that can predict the distribution of NPEs between pulp fibers, dissolved organic materials, inorganic precipitates, and ions in solution.[10,11,12] Key to the use of these programs is the need to establish the amounts of NPEs incoming with the wood fiber. The content of inorganic species in wood has been studied in northern Scandinavian wood samples, but few studies have examined the presence of NPEs in the southeastern US.[13,14,15] This report examines the distribution of NPEs for a series of softwood and hardwood kraft pulping operations in the southeastern US.

EXPERIMENTAL

Materials

All chemical reagents were commercially purchased and used as received. Commercial hardwood and softwood wood chips and kraft pulps were acquired from several mills in the state of Georgia. The pulps were collected from the mills at the end of brownstock washing line. In this study no attempt was made to time relate the collection of the wood chips and kraft pulps. All chips were extensively washed with Nano-pure water prior to acid-digestion and ICP analysis. Bark was removed from several wood chip samples, and this material was acid digested and analyzed for NPEs.

NPE Analysis of Wood, Bark, and Pulp

The chips (or bark or pulp) selected for analysis was exhaustively washed with Nano-pure water, the sample (approximately 2.0000 gr.) was then air-dried and acid digested following standard literature procedures.[16] In brief, this procedure employs concentrated nitric acid at elevated temperatures to hydrolyze the wood sample. The digested material is then analyzed for NPEs by a Perkin Elmer Optima 3000 DV ICP Emission Spectrometer. The results of these studies are summarized in Tables 1 –7.

RESULTS AND DISCUSSION

Despite the complexities of modeling NPE distributions through pulping and bleaching operations, the starting point for all these studies is the amounts of NPEs in the wood furnish. This study was directed at determining the levels of NPEs that occur in wood samples for various mills located in the southeastern US. SW and HW wood chip samples were acquired from eight commercial kraft operations. The wood chips were exhaustively washed with de-ionized water, acid-digested, and analyzed for metals by standard ICP techniques.

As an initial investigation of the NPEs in SW chips, we took approximately 2 gr. of wood chips and acid digested this material following literature procedures. Alternatively, 240 gr of dry SW chips were Wiley milled using a 200-mesh screen, the wood dust was thoroughly mixed, and a 2 gr. sample of milled wood was acid digested. The latter sample was generated based on the assumption that a greater sample mass of wood chips would yield a more representative measurement of NPE values in wood. The results of ICP analysis of SW wood chips and Wiley milled SW are summarized in **Table 1.**

Wood Sample/Metal:[1]	Na	K	Ca	Ba	Mg	Mn	Fe
Wood chips	17	111	462	1	146	11	1
Wiley milled	21	164	553	2	162	20	59

[1]NPE values presented as mg of metal/kg od wood.

I. NPE analysis of SW from woodchips and Wiley milled sawdust.

For the most part, the metals distribution from the wood chips and Wiley milled wood samples were very comparable. The Wiley milled material was found to have substantially elevated iron

values that were shown to be due to the milling process. In light of these results, all subsequent NPE studies were performed using wood chips.

Several mills provided samples of wood chips prepared at the mill (MC) and purchased chips (PC). The results of the ICP analysis for the SW wood chips are summarized in **Table 2**. The data reveal some interesting trends as all wood samples studied were found to have very low amounts of iron and barium. Typically, the amounts of sodium in the wood samples were only slightly greater than the quantified amounts of Fe or Ba. Of the metals studied in this project, calcium was the most predominant NPE and potassium was the second most prevalent.

The magnesium and manganese values were approximately half the calcium concentrations, with most SW samples having slightly more magnesium than manganese. Although our experimental scatter associated with these measurements was typically in the range of 10-30%, these standard deviation values were all acquired using the same wood chip. A key consideration when reviewing NPE values for wood chips is how these values may change over an extended period of time when differing wood samples are delivered to a mill. Although this issue cannot be fully determined in this study, we were able to examine this parameter by measuring NPEs in SW and HW wood chips from Mill F that were acquired in 1997. The results of this analysis are summarized in **Table 3**, and this data suggests that the variation NPEs in wood are not of the magnitude that they invalidate the results acquired in this study.

A total of five HW kraft pulping operations provided chip samples for NPE analysis. The wood chips were analyzed in much the same manner as the SW wood chips, and the results of this analysis are summarized in **Table 4**. The results of ICP analysis of HW wood chips samples suggested that the concentrations of NPEs in wood chips was approximately Ca> K> Mg> Mn > (Na, Ba) > Fe. Although the same pattern was observed in SW, all HW samples had higher absolute amounts of NPEs than were detected in SW samples. The experimental scatter in the HW samples was typically greater than that what was observed in the SW samples. This difference was attributed to the greater diversity in wood species contributing to HW wood chips. **Table 5** summarizes the metals profile found for gum and oak samples collected from one pulp mill woodyard operation. The factors contributing to these differences are unknown and require further study.

Wood[1]/ Metals:[2] Na	K	Ca	Ba	Mg	Mn	Fe	Si
A-PC1	10(1)	460 (23)	645(93)	2 (1)	244(11)	162 (9)	6 (1)	11(3)
A-PC2	15	290	650	4	205	102	1	8
A-PC3	19	223	759	2	135	67	2	7
A-PC4	6	462	743	8	216	71	8	10
A-PC5	4	225	446	8	120	95	4	17
A-PC6	8	284	455	5	138	98	2	10
A-PC7	8	570	616	3	288	29	18	19
A-PC8	7	282	663	3	231	61	6	19
B-MC	13	326	780	4	215	115	3	13
B-PC	13	180	710	3	161	66	8	14
C-PC	13	346	543	7	151	134	3	12
D-MC	32	190	723	5	149	17	7	7
D-PC	12	124	437	7	118	22	4	12
E-MC	29	485	642	3	192	44	5	22
E-PC	12	168	447	3	155	78	5	11
F-MC	8	246	652	12	195	75	2	16
G-MC	18(3)	111(33)	462(31)	1(1)	146(15)	11(1)	1(1)	18(1)
H-MC	36	298	616	5	227	15	2	13

[1]First letter represents the mill from which the sample was collected; MC=mill prepared wood chips, PC=purchased wood chips; [2]NPE values presented as mg of metal/kg od wood, values in the brackets are the standard deviation values determined by repeating acid hydrolysis/ICP procedure.

II. NPE analysis[1] of SW chips mill prepared and/or commercially purchased from woodyard operations.

Wood[1]/Metals: [2] Na	K	Ca	Ba	Mg	Mn	Fe	Si
SW							
F-MC(1999)	8	246	652	12	195	75	2	16
F-MC(1997)	5	287	527	8	139	91	3	8
HW							
F-MC(1999)	10	841	851	17	223	62	3	17
F-MC(1997)	15	799	1200	22	386	75	5	22

[1] First letter represents the mill from which the sample was collected; MC=mill prepared wood chips, PC=purchased wood chips; [2]NPE values presented as mg of metal/kg od wood

III. NPE analysis of 1999 and 1997 SW and HW mill prepared chips.

Wood[1]/Metals: [2]	Na	K	Ca	Ba	Mg	Mn	Fe	Si
B-MC	16	709	991	21	422	108	3	19
B-PC	30 (3)	592 (44)	2603 (181)	34 (2)	501 (127)	113 (19)	4 (1)	17 (8)
C-MC	47	889	1390	6	998	16	1	12
C-PC	90	749	1140	9	382	41	4	12
D-MC	97	477	1370	12	721	6	3	12
D-PC	29	1540	2350	9	130	49	12	8
F-MC	10 (3)	547 (93)	851 (17)	17 (5)	223 (24)	62 (13)	3 (1)	16 (4)
H-MC	65	467	1360	8	405	18	4	13

[1] First letter represents the mill from which the sample was collected; MC=mill prepared wood chips, PC=purchased wood chips; [2]NPE values presented as mg of metal/kg od wood, values in the brackets are the standard deviation values determined by repeating acid hydrolysis/ICP procedure.

IV. NPE analysis of HW chips mill prepared and/or commercially purchased from woodyard operations.

Wood Sample/Metal[1]	Na	K	Ca	Ba	Mg	Mn	Fe	Si
Oak	14	914	814	12	187	23	1	19
Gum	44	950	1240	16	858	17	1	12

[1] First letter represents the mill from which the sample was collected; NPE values presented as mg of metal/kg od wood.

V. NPE analysis[1] of oak and gum chips mill prepared.

All wood chips analyzed for NPEs were carefully selected to be bark free, as it is known[17] that bark contains significant amounts of NPEs. The presence of NPEs in the bark of the wood samples studied in this project was investigated using samples from mills A and F. The results of ICP analysis of these bark samples are summarized in **Table 6**. A comparison of the ICP bark data with the corresponding wood chips indicates that the bark samples had significant elevated levels of Ca, Mg, and K. Additional differences in metal contents were observed but these were SW and HW dependent. For mills encountering calcium or potassium-related problems, improved debarking procedures may be one approach to reducing the amounts of these metals being introduced into the mill.

Bark[1]/ Metals[2] Na	K	Ca	Ba	Mg	Mn	Fe	Si
Mill A							
PC1 (SW)	11	740	1,930	9	562	133	19	16
PC7 “”	10	3,750	1,700	4	981	32	18	36
PC8 “”	11 (3)	631 (74)	2,255 (695)	7 (1)	503 (160)	37 (7)	32 (13)	34 (9)
Mill F								
MC-SW	24	1,270	2,020	26	915	143	14	15
MC-HW	48	1,510	50,200	624	1,000	682	28	112

[1] MC=mill prepared wood chips, PC=purchased wood chips; [2]NPE values presented as mg of metal/kg od bark, values in the brackets are the standard deviation values determined by repeating acid hydrolysis/ICP procedure.

VI. NPE analysis of HW and SW bark samples from mill prepared wood chips

NPEs in Pulps

Typically, the kraft pulping process is the first chemical process that can alter the composition of NPEs in wood fibers. The profile of NPEs in kraft fibers are a result of many process parameters, including the metals in the wood, metals in the green liquor, cooking chemistry, and the pulping process employed. Given these considerations, it was of interest to determine how the NPEs levels of wood compared against those of the pulp. **Table 7** summarizes the NPE levels of several kraft pulps.

Pulp Sample[1]/Metal[2] Na	K	Ca	Ba	Mg	Mn	Fe	Si
A-SW	1,330	69	1,030	7	263	77	5	141
F-SW pulp	2,835 (21)	545 (6)	1,575 (134)	14 (1)	314 (1)	91 (1)	27 (1)	96 (30)
F-HW pulp	1,290 (28)	244 (4)	2,065 (50)	31 (1)	321 (10)	64 (2)	20 (3)	88 (10)
H-SW pulp	472	11	1,390	4	472	40	14	78
H-HW pulp	549	7	3,550	28	549	24	7	74

[1]First letter represents the mill from which the samples was collected; [2]NPE values presented as mg of metal/kg od pulp, values in the brackets are the standard deviation values determined by repeating acid hydrolysis/ICP.

VII. NPE analysis[1] of mill HW and SW kraft pulp samples.

The results of the NPE studies for the kraft pulps indicates that the NPE values in the wood chips are mirrored, to some extent, in the pulps, but clearly a variety of pulping process parameters influence the overall metals content of the pulps. It is interesting to note that the barium and iron concentrations remain low relative to the other metals in the kraft pulps.

CONCLUSIONS

The NPE studies in this report suggest a commonality to metal profiles in the SW and HW wood chips acquired from mills in the southeastern US. This is undoubtedly due, in part, to the soil chemistry from which the tree samples were collected. Our results suggest that HW samples introduce more NPEs into the pulping process than SW fiber. Inefficient debarking will also be another source of metals into the mill as the amounts of metals in HW and SW barks are much higher than in the wood itself. Although the NPEs in the incoming wood chips contributes to the NPE profile of the mill, the mill operations have a tremendous influence on the NPE profiles of kraft pulps. In the modeling of NPEs in a pulp mill, all these factors will have to be taken into account.

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