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THE EFFECT OF D STAGE PH ON EFFLUENT QUALITY: CHARACTERIZATION OF EFFLUENT FRACTIONS FROM OD(EO) BLEACHING OF SOFTWOOD KRAFT PULP

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ABSTRACT

Effluents from OD(EO) laboratory bleaching of soft-wood kraft pulp were characterized by fractionation and analysis of the fractions. The fractionation consisted of ether extraction followed by separation of the extract into acidic, phenolic, and neutral subfractions. The effluents from the sequence with the D stage begun at pH 2 (D-2 bleaching) were compared to the same sequence with the D stage begun at pH 4 (D-4 bleaching). Adsorbable organic halide (AOX) and total organic carbon (TOC) were determined for the whole D and (EO) effluents as well as for the fractions from both stages. Each fraction was characterized in terms of its ratio of chlorine to carbon (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}) and in terms of the proportion of total TOC within each fraction. The Cl/C_{100} is a likely predictor of environmental effects caused by certain effluent fractions.

The D-4 bleaching resulted in a reduced kappa number in the extracted pulp compared to the D-2 case. This is consistent with the whole effluent TOC data, in which D-4 bleaching produced more D stage TOC than the D-2. The (EO) stage TOC remained constant. The chlorine-to-carbon ratio decreased for each effluent type when D-4 bleaching was done.

The ether extractable material and the phenolic fraction, which both contain compounds of environmental interest, exhibited reduced Cl/C_{100} values when D-4 bleaching was done. Since the percentage of total TOC within these fractions increased, overall AOX levels were nearly constant, however. Because of the greater delignification at D-4 conditions, environmental and economic benefits may be realized by a reduction of the applied ClO_2 charge.

INTRODUCTION

It is generally accepted that bleaching at a pH of 2 or less results in greater delignification effectiveness for chlorine bleaching (1), for mixtures of chlorine and chlorine dioxide (2), and for chlorine dioxide alone (2, 3, 4, 5). However, an initial pH above 2 may be more effective in some cases (2, 3, 6).

The pH of a chlorination stage also has an effect on the quality of the effluent produced in the stage. The rates of formation of both chlorinated dioxins (7, 8) and chlorinated phenolic compounds (9, 10) are reduced by increased C stage pH. Total AOX is reduced at increased pH for both chlorine and chlorine dioxide bleaching (2).

Pulp bleaching effluents in general have been characterized with respect to adsorbable organic halide (AOX) (11-15) and in terms of individual compounds or environmentally significant groups of compounds such as chlorophenolics (9, 10, 15-21), chlorinated dioxins (7, 8, 18), chlorinated neutral compounds (21-23), chlorinated carboxylic acids (21, 24), and chloroform (17, 25).

Because of the complexity of pulp bleaching effluents, these analyses give an incomplete picture of their likely environmental effects. An alternative is summative analysis of the effluent by fractionation into meaningful classes of compounds, followed by relevant characterization of the fractions. One such procedure, based on ether extraction, has been developed and applied to effluents produced by D(EO), OD(EO), and OC(EO) sequences (26). Ether extraction was chosen as the basis for this procedure because virtually all effluent components known to be significant from an environmental standpoint are found in the extracts. Chlorine-to-carbon ratios (expressed as the number of chlorine atoms per hundred carbon atoms, Cl/C_{100}), which may predict environmental behavior, were determined for the fractions. The same fractionation and characterization methods were used for the present study of the effects of D stage initial pH in OD(EO) bleaching of softwood kraft pulp.

EXPERIMENTAL APPROACH

Pulp Bleaching

A mill-produced, oxygen-bleached kraft pulp with a kappa number of 14.1 was bleached by an OD(EO) sequence in the laboratory. Only the first two stages of bleaching were done, since most of the delignification and most of the effluent load production occurs in these stages. The D stages were done in a specially designed batch reactor, and the (EO) stages were done in a high shear mixer. The pH of the pulp slurry was adjusted to an initial level of 2 or 4 by the addition of sulfuric acid solution. Kappa numbers after bleaching are given in Table I.

Effluent Fractionation and Characterization

The effluents produced in this study were fractionated by ether extraction, and the ether extractable material was further separated into acidic, phenolic, and neutral fractions. To measure Cl/C_{100} on the ether extract and its fractions, the ether was exhaustively removed by evaporation, and AOX and TOC were then measured on each fraction. During evaporation, volatiles other than ether were also removed. To obtain information on the volatile fraction, a sample of the whole effluent was similarly evaporated and the carbon and chlorine losses determined.

Figure 1 depicts the effluent fractionation scheme, and Table II lists the names or codes of all effluent fractions and provides an explanation of each. The bleaching effluents were extracted with ether in continuous liquid-liquid extractors. Two successive extractions were performed, resulting in three fractions: a non-extractable fraction and two ether extractable fractions. The first ether fraction is material readily extracted, and the second is removed slowly over an extended period. The first was further fractionated into acids, phenolics, and neutrals. Each fraction was then evaporated, as represented in Figure 1 by the dashed horizontal lines, to yield the final samples.

Data Analysis

The D-2 and D-4 bleaching sequences were performed in duplicate, and the effluents from the D and (EO) stages of bleaching were fractionated and analyzed separately. This resulted in two completely independent sets of data for each sequence. The data for all fractions are given in Tables III-X. The total TOC and AOX (given in Table III) represent TOC and AOX mass balances around the fractionation scheme, and were determined as the sums of the AOX and TOC measurements for the neutral, phenolic, acidic, polar, hydrophilic, and volatile fractions.

The data for individual fractions were interpreted principally in terms of their Cl/C_{100} values and their relative sizes, expressed as a percentage of total TOC. The Cl/C_{100} is of interest as a likely predictor of lipophilicity and toxicity within certain fractions.

Analyses of variance (AOV) were done on the data from each fraction to assess the significance of differences between pH levels and between stages. Since data with high Cl/C_{100} had a greater variance than the low Cl/C_{100} data, all Cl/C_{100} data were log transformed to stabilize variance. When AOV showed a significant effect between pH levels, a least significant difference was determined using Duncan's multiple range test (27).

RESULTS AND DISCUSSION

Whole Effluents

Data for the whole effluents are presented in Table III. The whole effluents contain 3.8-7.0 kg/t TOC and 0.1-0.4 kg/t AOX, depending on the stage and initial D stage pH.

Figure 2 compares mean effluent TOC from OD(EO) bleaching with the D stage begun at pH 4 (D-4 bleaching) and from the same sequence with the D stage begun at pH 2 (D-2 bleaching). In the D stage, and overall, the D-4 case results in the production of more effluent TOC. There is no increased TOC production in the (EO) stage following D-4 bleaching. A reduced kappa number is observed for the pulp from D-4 bleaching and could correspond to the higher level of TOC in the D stage effluent. The delignification of the pulp is discussed later in more detail.

Figure 3 presents a comparison of mean Cl/C_{100} for the whole effluents. Both the D and (EO) stage effluents individually have a greater Cl/C_{100} when D-2 bleaching is done. No overall difference is seen, however.

Ether Soluble Fraction

Table IV presents detailed data for the ether soluble fraction. This fraction contains 0.3-0.7 kg/t TOC, rep-

resenting 6-12% of the total TOC, and 0.01-0.08 kg/t AOX, representing 14-23% of the total AOX.

Figure 4 presents the mean ether soluble TOC as a percentage of total TOC for both pH levels. The mean TOC produced by D-4 bleaching is greater for each stage. Although the difference is not great enough to be statistically significant when all data are used, when the calculated value (see Table IV) is not included in the analysis, the difference is significant. This calculated value was eliminated from analysis because it is likely to contain greater error than measured values. It was determined from several measured values, each with individual errors.

Figure 5 similarly compares both pH levels with respect to Cl/C_{100}. The ether soluble fraction is chlorinated to a larger extent in both the D and (EO) stages when D-2 bleaching is done.

The reduced level of substitution by chlorine on organic material could be the result of a shift in chlorine containing species at pH 4 versus pH 2. Kolar and co-workers (28) reported that the sum of Cl_2 and $HOCl$ during ClO_2 bleaching at pH 4.5 was reduced compared with similar bleaching at pH 2.5. Since Cl_2 and $HOCl$ are responsible for chlorine substitution reactions (29, 30), an overall reduction in the level of these species would result in less substitution by chlorine atoms on organics in the effluent.

In addition to a reduction in the sum of Cl_2 and $HOCl$ concentrations, a change in their ratio will occur. The $Cl_2/HOCl$ equilibrium is such that $HOCl$ is more favored as pH increases.

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$
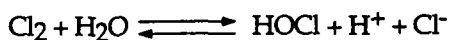
As acidity decreases, the equilibrium shifts to the right and to $HOCl$. Therefore, at pH 4 a greater proportion of the total chlorine exists as $HOCl$ than at pH 2. Since $HOCl$ is a less reactive chlorinating species (31), a reduced degree of chlorine substitution is expected at pH 4.

It is reasonable that a change in substitution behavior with pH will be more clearly seen in the ether soluble fractions. Chlorine substitutes to a greater extent on ether extractable material than on whole effluents (26). Therefore, these fractions are probably more sensitive to changes in substitution behavior than the whole effluents.

Since there is more ether soluble material formed by D-4 bleaching and that material is chlorinated to a reduced extent, the overall AOX remains essentially constant under both sets of conditions. This trend is repeated in other ether extractable fractions as well. This is consistent with the decreased tendency of ClO_2 to be involved in substitution of chlorine atoms at pH 4 and with the increased lignin fragmentation seen at pH 4, as indicated by the reduced kappa number achieved at constant chemical charge. Increased lignin fragmentation could be responsible for a greater proportion of material in the ether soluble fractions.

Phenolic Fraction

Detailed results of the analysis of the phenolic fraction are shown in Table V. The phenolic fraction contains 0.02-0.05 kg/t TOC or 0.5-0.7% of the total TOC, and 0.002-0.003 kg/t AOX or 0.8-2.6% of the total AOX.

Figure 6 compares the phenolic TOC as a percentage of total TOC for the two pH levels. In both the D and (EO) effluents, the phenolic fraction represents a higher percentage of the total TOC when the D stage is conducted at pH 4. Figure 7 shows the effect of pH on Cl/C_{100}. A decreased phenolic Cl/C_{100} is seen in the D-4 case.

Other Fractions

Data from the other effluent fractions displayed no statistically significant pH effects. This was generally due to small differences in means and scatter in the replicate data. Data and graphs for these fractions are provided so that the characterization is complete, and so that trends in the data may be observed. Replicate data for the neutral, acid, polar, hydrophilic, and the volatile fractions are provided in Tables VI-X. The corresponding graphs of the mean data are given in Figures 8-17.
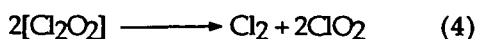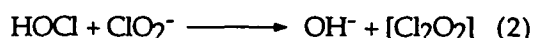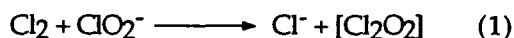
It is interesting to note, that despite the lack of statistical significance, the other ether soluble fractions often maintain the trend observed with the ether soluble and phenolic fractions. On the average, the neutral, acid, and polar fractions all appear to contain a larger proportion of the total TOC when bleaching is conducted at pH 4, while the overall mean Cl/C_{100} is lower under D-4 conditions for the acid and polar fractions. Since a larger percentage of the material is extracted from effluents produced with D-4 bleaching, it is expected that the mean proportion of non-

extractable TOC should be lower under D-4 conditions (Figure 14), as is the case.

Degree of Delignification

The D stage effluent contains more TOC when the D stage is conducted at an initial pH of 4. The kappa number of the extracted pulp is reduced to 3.7 under D-4 conditions compared with 4.3 under D-2 conditions. The D+(EO) stage TOC, the kappa numbers, the change in pulp kappa number, and the ratio of TOC to kappa change are all given in Table I for the two pH levels. In an earlier study (26), it was stated that increased TOC per unit kappa loss may imply greater carbohydrate loss. Although the D stage begun at pH 4 appears to give slightly increased TOC per unit kappa loss, the apparent difference is not statistically significant.

In D-4 bleaching more delignification or kappa reduction can be done because less of the oxidizing power of ClO_2 may be wasted on other reaction types such as chlorine substitution reactions and chlorate (ClO_3^-) formation. A reaction byproduct of the oxidation of lignin by ClO_2 is chlorite ion (ClO_2^-) which may form chlorate or chlorine dioxide, depending on conditions, by the following reaction scheme (32, 33):

$$Cl_2 + ClO_2^- \longrightarrow Cl^- + [Cl_2O_2] \quad (1)$$

$$HOCl + ClO_2^- \longrightarrow OH^- + [Cl_2O_2] \quad (2)$$

$$[Cl_2O_2] \longrightarrow Cl^- + ClO_3^- \quad (3)$$

$$2[Cl_2O_2] \longrightarrow Cl_2 + 2ClO_2 \quad (4)$$

A high concentration of the reactive intermediate $[Cl_2O_2]$ favors the formation of ClO_2 by reaction 4 (second order in $[Cl_2O_2]$). Since chlorite ion is present in higher concentrations during pulp bleaching at pH 4 compared to pH 2 (28), reactions 1 and 2 (both first order in ClO_2^-) will produce increased levels of $[Cl_2O_2]$ at pH 4 and therefore more ClO_2 will be produced by reaction 4.

EXPERIMENTAL METHODS

Pulp Bleaching

A mill-produced, 14.1 kappa O_2-delignified southern softwood kraft pulp was used in this study. The pulp was collected just after the O_2 stage and was well washed before bleaching.

D Stages.

All D stages were done in a specially designed 20 L batch reactor. Bleaching was done at 2% consistency, at 45°C, for 30 minutes, and at a kappa factor of 0.25. The mixer was run at 350 rpm. Initial pH was adjusted to 2 or 4 by the addition of sulfuric acid solution.

(EO) Stages.

All (EO) stages were done in a Quantum Technologies high shear mixer at 10% consistency, at 70°C, and for 70 minutes. The NaOH charge was 0.55 times the total active chlorine charge; the O_2 charge was 0.5% on pulp; and 4.1% of the total D stage filtrate was included as carryover. The slurry was mixed at 15 hertz for 3 seconds, every 5 minutes.

Effluent Preparation

The D stage effluent was collected by filtration of the 2% slurry; the (EO) stage effluent was similarly collected after the 10% slurry was diluted to 2%. This was done to maintain a similar TOC content in all effluents for ether extraction. Effluent samples were filtered to remove any fibers, quenched with excess sodium sulfite, and acidified to a pH of less than 2. Ether extractions were always started within 2 days of effluent collection.

Ether Extraction of Effluents

Ether extraction was done on 4 L of effluent using continuous liquid-liquid extractors. Extraction was carried out with 500 ml of diethyl ether. The first ether phase was collected after 96 hours of extraction and was replaced with 500 ml of fresh ether. Extraction was continued for 336 total hours. The extraction was then stopped, and the second ether phase and the non-extractable materials were collected.

Ether Extract Fractionation

The first ether phase was diluted to 500 ml, 100 ml of the sample collected, and the remaining ether placed in a separatory funnel for fractionation. The ether was extracted 3 times with 25 ml of 0.5 M NaHCO3, and the extracts were collected and acidified. The ether was next extracted 3 times with 25 ml of 0.5 M

NaOH, and these extracts were also collected and acidified. The NaHCO3 soluble material is the acidic fraction; the NaOH soluble material is the phenolic fraction; and the remaining ether soluble material is the neutral fraction.

Sample Preparation

Ether was removed from all samples by evaporation to dryness, or near to dryness. The samples were then dissolved in water, acidified, and diluted to a known volume. To ensure reasonable sample recovery and to be certain the ether was removed, TOC and AOX mass balances were done around the fractionation scheme.

TOC Analysis

Measurement of TOC was done using a Beckman model 915-B Tocamaster analyzer. The instrument was calibrated using standard solutions of potassium hydrogen phthalate. Samples were prepared for TOC analysis by acidifying them, and sparging for 5 minutes with nitrogen to drive off any interfering carbonate species.

AOX Analysis

Measurement of AOX was done using a Dohrman model DX-20 organic halide analyzer. Sample preparation was done by a slight modification of method SCAN-W 9:89 (34). In this case samples were shaken for 4 hours rather 1 hour, to more completely adsorb the polar fractions.

SUMMARY AND CONCLUSIONS

An oxygen-bleached softwood kraft pulp was delignified to a greater extent by the OD(EO) sequence when the D stage was run at an initial pH of 4 compared to an initial pH of 2. D-4 bleaching resulted in a greater percentage of the total TOC within the environmentally significant ether soluble and phenolic fractions. However, the material within these fractions was substituted by chlorine atoms to a reduced extent under D-4 conditions. The net result was similar amounts of AOX at both pH levels.

Since D-4 bleaching causes increased D stage delignification, an equivalent amount of delignification can be done with less applied chemical, and an economic gain achieved. A reduced ClO_2 charge will result in less effluent AOX. Reducing the charge may also re-

duce the extent of lignin fragmentation and may reduce the proportion of material within the ether soluble fractions. If this proportion were reduced, the lower Cl/C_{100} values observed under D-4 conditions would represent a clear environmental advantage.

ACKNOWLEDGMENTS

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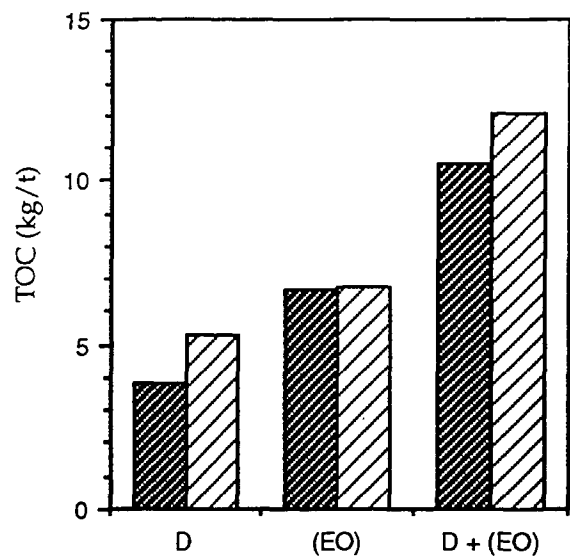
Figure 1. Effluent Fractionation.
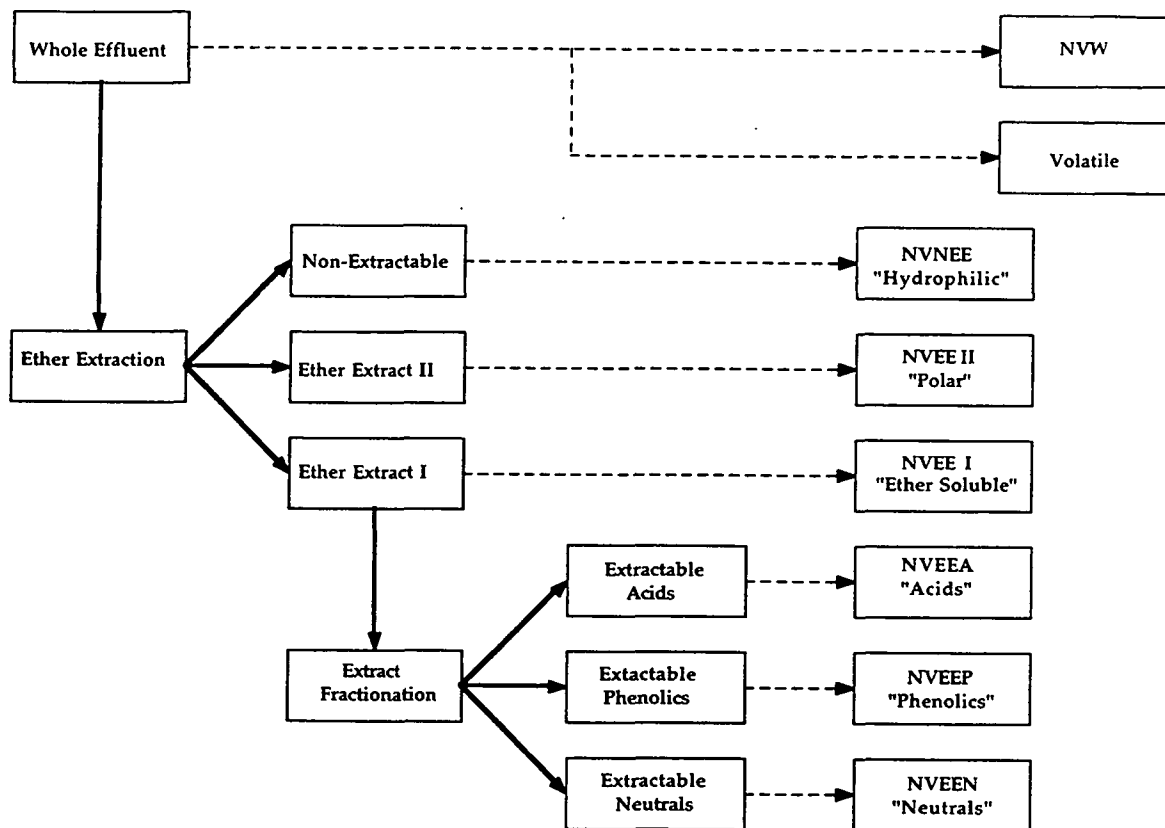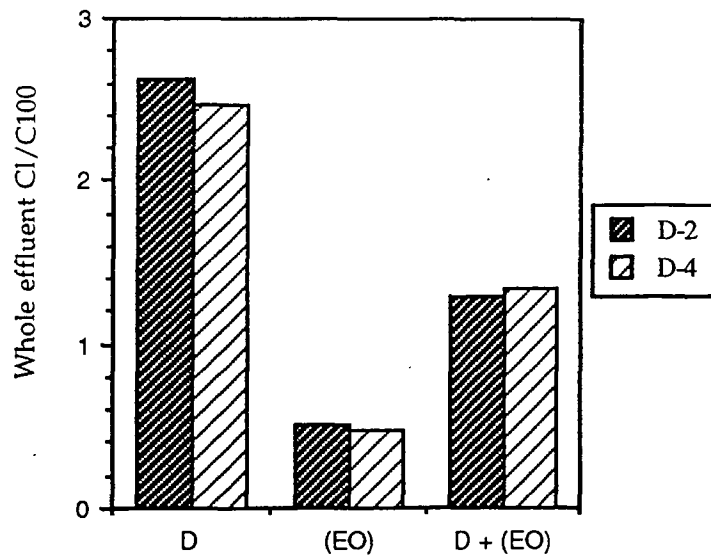
Figure 2. Whole effluent TOC.

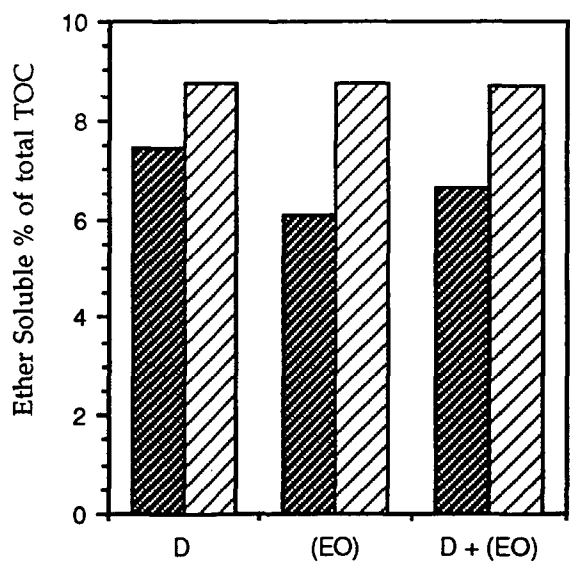Figure 3. Whole effluent Cl/C100.

Figure 4. Ether Soluble % of total TOC.
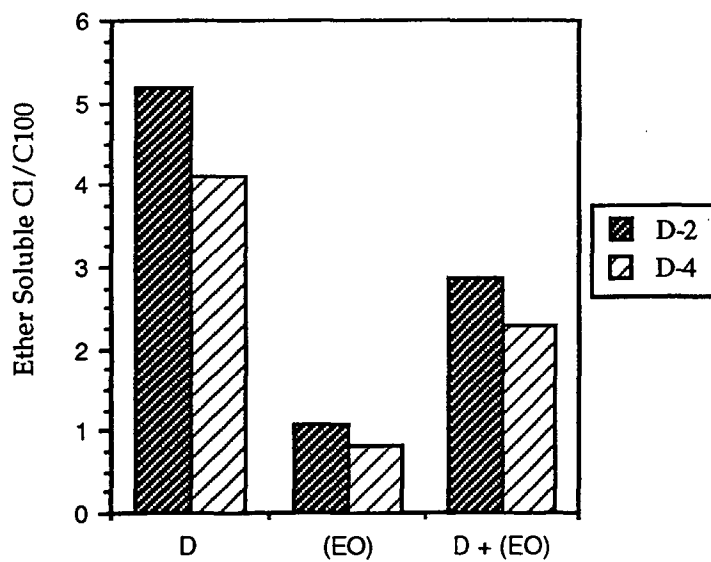
Figure 5. Ether Soluble Cl/C100.
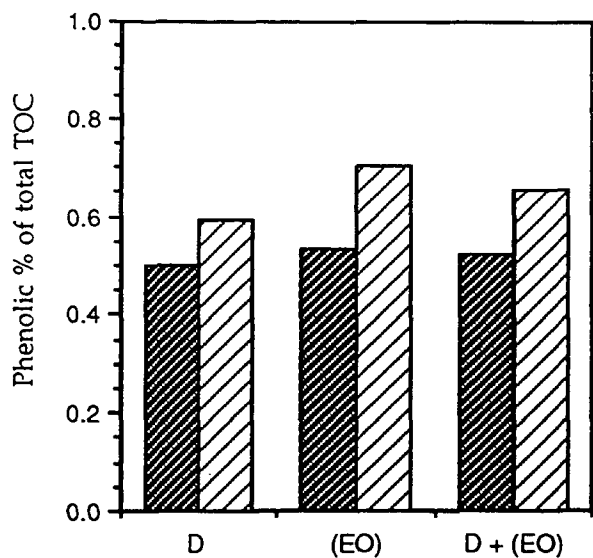
Figure 6. Phenolic % of total TOC.

Figure 7. Phenolic Cl/C100.

Figure 8. Neutral % of total TOC.

Figure 9. Neutral Cl/C100.
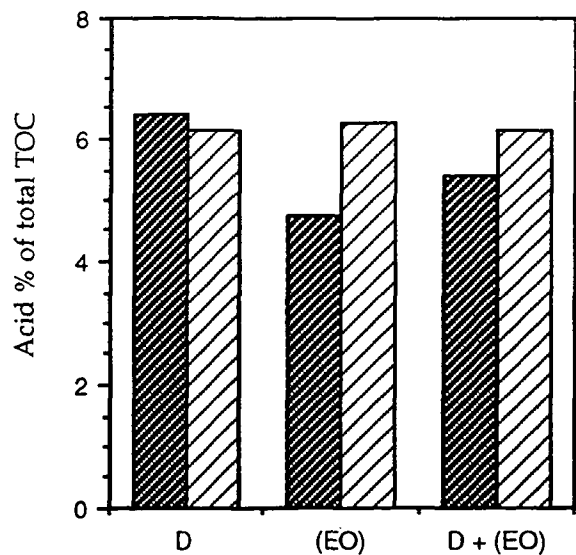
Figure 10. Acid % of total TOC.
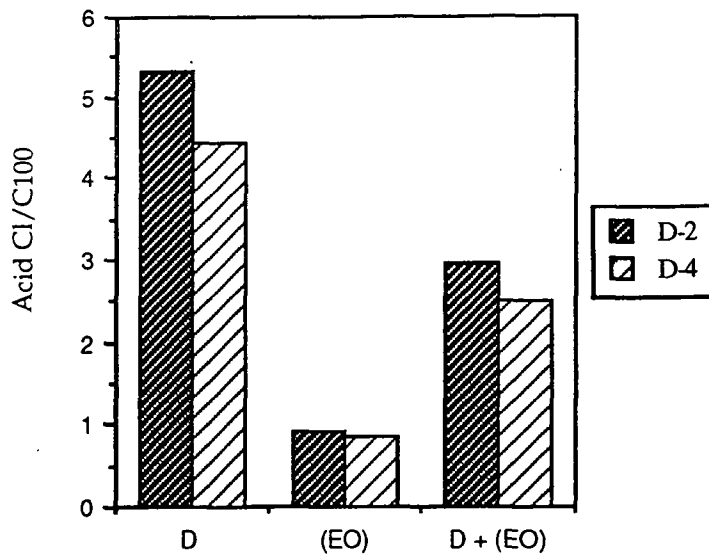
Figure 11. Acid Cl/C100.
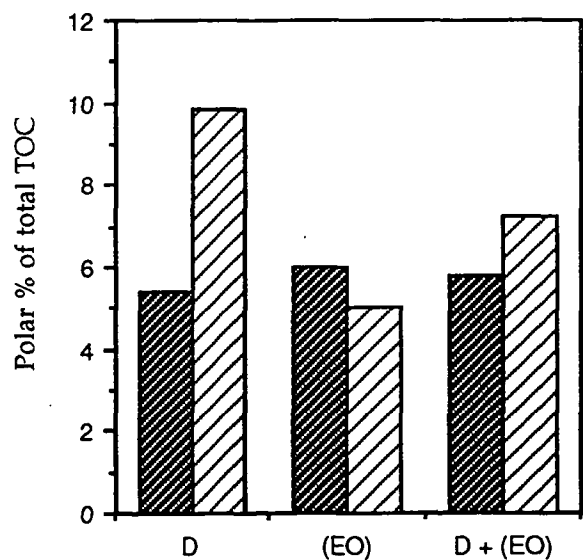
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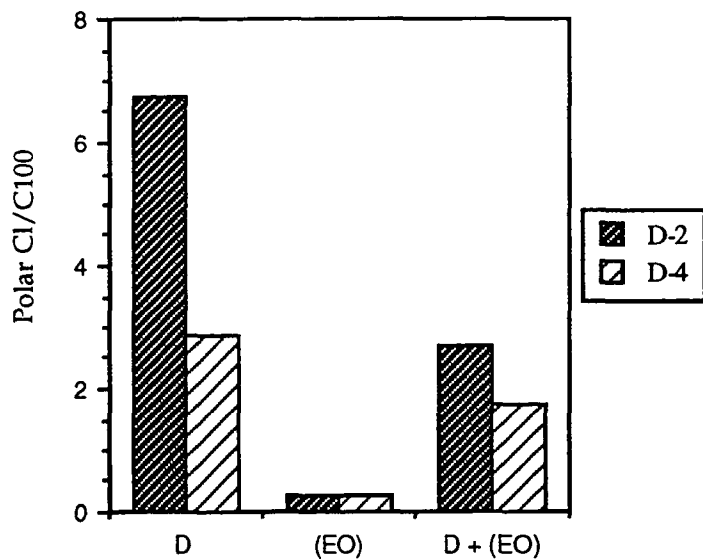
Figure 13. Polar Cl/C100.
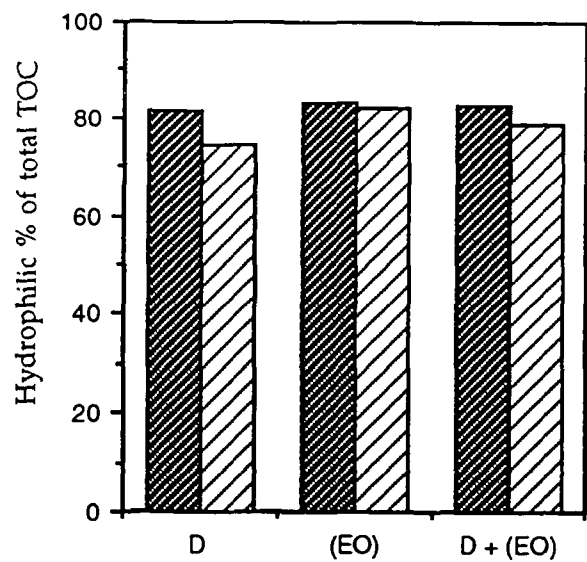
Figure 14. Hydrophilic % of total TOC.
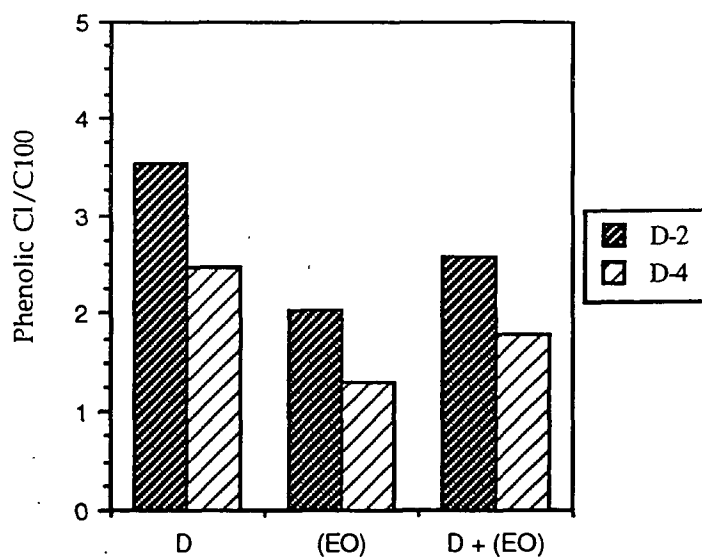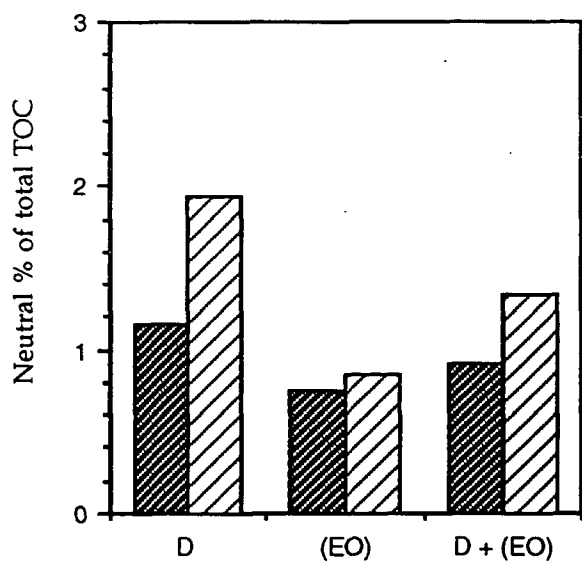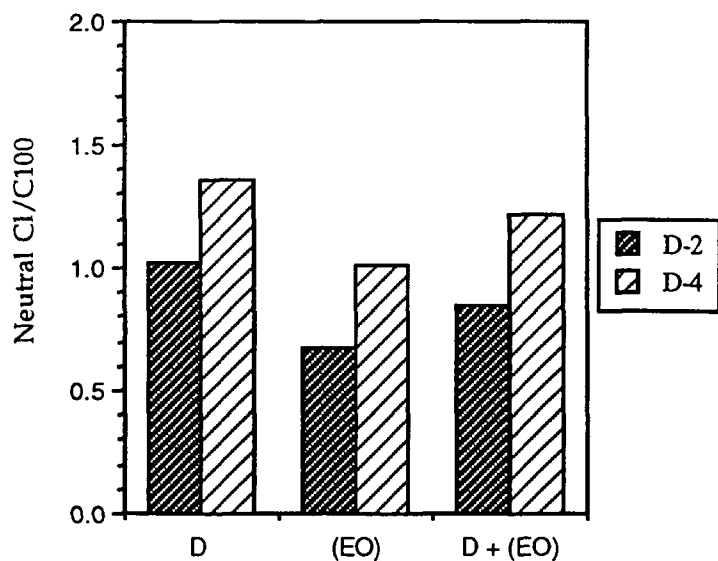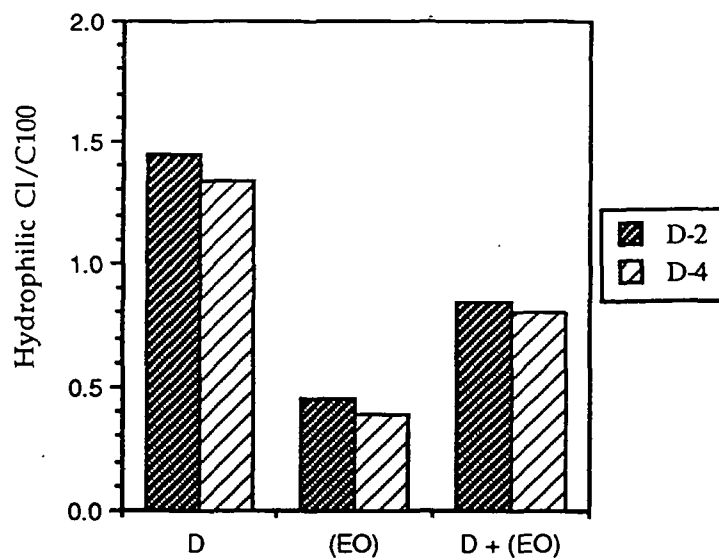

Figure 15. Hydrophilic Cl/C100.
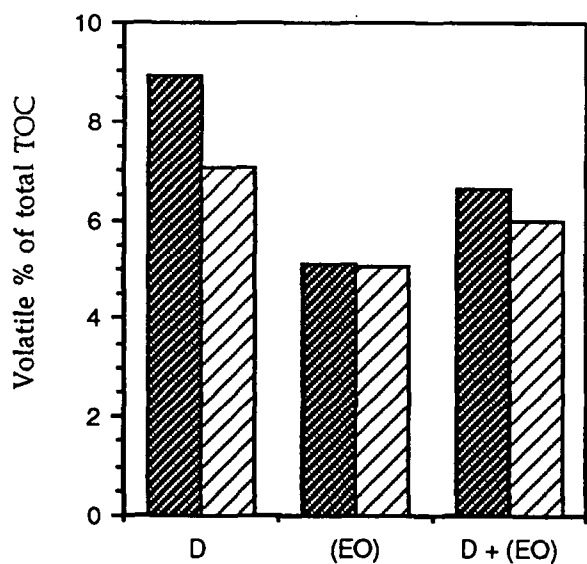
Figure 16. Volatile % of total TOC.
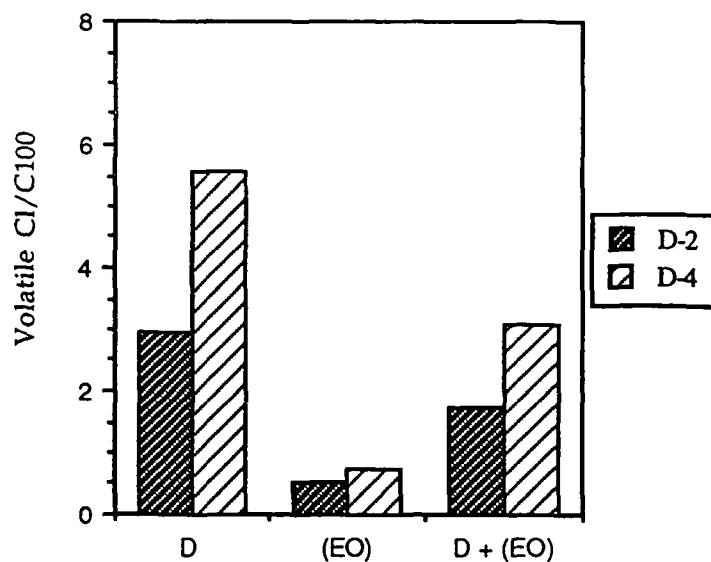
Figure 17. Volatile Cl/C100.

Table I. D+(EO) TOC and Kappa Number Data for OD(EO) Sequence.

D Stage Type	D + (EO) TOC (kg/t)	Kappa Number	Δ kappa	TOC/Δ kappa
D-2	10.6	4.23	9.87	1.07
D-2	10.4	4.44	9.66	1.08
D-4	12.4	3.70	10.40	1.19
D-4	11.7	3.71	10.39	1.13

Table II. Effluent Fraction Codes and Descriptions of Fractions.

Fraction Code	Description
NVW	Non-volatile, whole.
NVNEE	Non-volatile, non-ether extractable ("Hydrophilic").
NVEE II	Non-volatile, difficult to extract with ether ("Polar").
NVEE I	Non-volatile, readily ether extractable ("Ether Soluble").
NVEEA	Non-volatile, ether extractable acidic compounds ("Acids").
NVEEP	Non-volatile, ether extractable phenolic compounds ("Phenolics").
NVEEN	Non-volatile, ether extractable neutral compounds ("Neutrals").

Table III. Whole Effluent and Summed Fraction Characteristics.

D Stage	pH 2		pH 4	
TOC, kg/t	3.85	3.80	5.37	5.17
Total TOC[a], kg/t	4.43	4.29	5.55	6.64
AOX, kg/t	0.299	0.294	0.381	0.386
Total AOX[a], kg/t	0.297	0.264	0.337	0.336
Cl/C_{100}	2.63	2.61	2.40	2.53
(EO) Stage				
TOC, kg/t	6.79	6.60	7.01	6.54
Total TOC[a], kg/t	6.70	6.52	6.99	7.60
AOX, kg/t	0.101	0.102	0.0943	0.0929
Total AOX[a], kg/t	0.0938	0.0930	0.0983	0.0877
Cl/C_{100}	0.50	0.52	0.45	0.48
D Stage + (EO) Stage				
TOC, kg/t	10.6	10.4	12.38	11.71
Total TOC[a], kg/t	11.1	10.8	12.54	14.24
AOX, kg/t	0.400	0.396	0.475	0.479
Total AOX[a], kg/t	0.391	0.357	0.435	0.424
Cl/C_{100}	1.27	1.29	1.30	1.38

[a]Sum of corresponding values for volatile, hydrophilic, polar, acid, phenolic, and neutral fractions.

Table IV. Ether Soluble Fraction.

D Stage	pH 2		pH 4	
TOC, kg/t	0.383	0.267	0.643	0.388[a]
% of total TOC	8.65	6.22	11.6	5.85[a]
AOX, kg/t	0.0547	0.0439	0.0773	0.0474
% of total AOX	18.4	16.6	22.9	14.1
Cl/C_{100}	4.83	5.56	4.07	4.13[a]
(EO) Stage				
TOC, kg/t	0.406	0.399	0.532	0.748
% of total TOC	6.06	6.12	7.61	9.84
AOX, kg/t	0.0127	0.0125	0.0150	0.0154
% of total AOX	13.5	13.4	15.3	17.6
Cl/C_{100}	1.06	1.06	0.95	0.69
D Stage + (EO) Stage				
TOC, kg/t	0.789	0.666	1.175	1.136[a]
% of total TOC	7.09	6.16	9.37	7.98[a]
AOX, kg/t	0.0674	0.0564	0.0923	0.0628
% of total AOX	17.2	15.8	21.2	14.8
Cl/C_{100}	2.89	2.86	2.66	1.87[a]

[a]Determined from TOC balances. Sample was contaminated during evaporation.

Table V. Phenolic Fraction.

D Stage	pH 2		pH 4	
TOC, kg/t	0.0239	0.0198	0.0325	0.0389
% of total TOC	0.54	0.46	0.59	0.59
AOX, kg/t	0.00255	0.00201	0.00273	0.00239
% of total AOX	0.86	0.76	0.81	0.71
Cl/C_{100}	3.60	3.45	2.84	2.07
(EO) Stage				
TOC, kg/t	0.0364	0.0341	0.0513	0.0502
% of total TOC	0.54	0.52	0.73	0.66
AOX, kg/t	0.00243	0.00180	0.00216	0.00177
% of total AOX	2.59	1.94	2.20	2.02
Cl/C_{100}	2.26	1.79	1.42	1.19
D Stage + (EO) Stage				
TOC, kg/t	0.0603	0.0539	0.0838	0.0891
% of total TOC	0.54	0.50	0.67	0.63
AOX, kg/t	0.00498	0.00381	0.00489	0.00416
% of total AOX	1.27	1.07	1.12	0.98
Cl/C_{100}	2.79	2.39	1.97	1.58

Table VI. Neutral Fraction.

D Stage	pH 2		pH 4	
TOC, kg/t	0.0551	0.0457	0.175	0.0483
% of total TOC	1.24	1.07	3.15	0.73
AOX, kg/t	0.00153	0.00148	0.00350	0.00290
% of total AOX	0.52	0.56	1.04	0.86
Cl/C_{100}	0.94	1.09	0.68	2.03

(EO) Stage				
TOC, kg/t	0.0511	0.0480	0.0885	0.0313
% of total TOC	0.76	0.74	1.27	0.41
AOX, kg/t	0.00129	0.000701	0.00202	0.00114
% of total AOX	1.38	0.75	2.05	1.30
Cl/C_{100}	0.85	0.49	0.78	1.23

D Stage + (EO) Stage				
TOC, kg/t	0.106	0.0937	0.264	0.0796
% of total TOC	0.95	0.87	2.10	0.56
AOX, kg/t	0.00282	0.00218	0.00552	0.00404
% of total AOX	0.72	0.61	1.27	0.95
Cl/C_{100}	0.90	0.79	0.71	1.72

Table VII. Acid Fraction.

D Stage	pH 2		pH 4	
TOC, kg/t	0.316	0.242	0.428	0.301
% of total TOC	7.13	5.64	7.71	4.53
AOX, kg/t	0.0511	0.0369	0.0627	0.0350
% of total AOX	17.2	14.0	18.6	10.4
Cl/C_{100}	5.46	5.15	4.95	3.92
(EO) Stage				
TOC, kg/t	0.304	0.321	0.340	0.578
% of total TOC	4.54	4.92	4.86	7.61
AOX, kg/t	0.00856	0.00827	0.0105	0.0115
% of total AOX	9.13	8.89	10.7	13.1
Cl/C_{100}	0.95	0.87	1.04	0.67
D Stage + (EO) Stage				
TOC, kg/t	0.620	0.563	0.768	0.879
% of total TOC	5.57	5.21	6.12	6.17
AOX, kg/t	0.0597	0.0452	0.0732	0.0465
% of total AOX	15.3	12.7	16.8	11.0
Cl/C_{100}	3.25	2.71	3.22	1.79

Table VIII. Polar Fraction.

D Stage	pH 2		pH 4	
TOC, kg/t	0.226	0.248	0.386	0.848
% of total TOC	5.10	5.78	6.95	12.8
AOX, kg/t	0.0445	0.0502	0.0498	0.0336
% of total AOX	15.0	19.0	14.8	10.0
Cl/C_{100}	6.67	6.85	4.37	1.34
(EO) Stage				
TOC, kg/t	0.399	0.395	0.316	0.424
% of total TOC	5.96	6.06	4.52	5.58
AOX, kg/t	0.00333	0.00280	0.00269	0.00226
% of total AOX	3.55	3.01	2.74	2.58
Cl/C_{100}	0.28	0.24	0.29	0.18
D Stage + (EO) Stage				
TOC, kg/t	0.625	0.643	0.702	1.272
% of total TOC	5.62	5.95	5.60	8.93
AOX, kg/t	0.0478	0.0530	0.0525	0.0359
% of total AOX	12.2	14.8	12.1	8.46
Cl/C_{100}	2.59	2.79	2.53	0.95

Table IX. Hydrophilic Fraction.

D Stage	pH 2		pH 4	
TOC, kg/t	3.43	3.69	4.25	4.79
% of total TOC	77.4	86.0	76.6	72.1
AOX, kg/t	0.144	0.160	0.152	0.206
% of total AOX	48.5	60.6	45.1	61.3
Cl/C_{100}	1.42	1.47	1.21	1.46

(EO) Stage				
TOC, kg/t	5.50	5.45	5.84	6.13
% of total TOC	82.1	83.6	83.5	80.7
AOX, kg/t	0.0728	0.0745	0.0714	0.0644
% of total AOX	77.6	80.1	72.6	73.4
Cl/C_{100}	0.45	0.46	0.41	0.36

D Stage + (EO) Stage				
TOC, kg/t	8.93	9.14	10.09	10.92
% of total TOC	80.2	84.6	80.5	76.7
AOX, kg/t	0.217	0.235	0.223	0.270
% of total AOX	55.5	65.8	51.4	63.8
Cl/C_{100}	0.82	0.87	0.75	0.84

Table X. Volatile Fraction.

D Stage	pH 2		pH 4	
TOC, kg/t	0.380	0.396	0.276	0.609
% of total TOC	8.58	9.23	4.97	9.17
AOX, kg/t	0.0533	0.0136	0.0658	0.0557
% of total AOX	17.9	5.15	19.5	16.6
Cl/C_{100}	4.74	1.16	8.06	3.09
(EO) Stage				
TOC, kg/t	0.405	0.271	0.352	0.384
% of total TOC	6.04	4.16	5.04	5.05
AOX, kg/t	0.00539	0.00490	0.00956	0.00662
% of total AOX	5.75	5.27	9.73	7.55
Cl/C_{100}	0.45	0.61	0.92	0.58
D Stage + (EO) Stage				
TOC, kg/t	0.785	0.667	0.628	0.993
% of total TOC	7.05	6.17	5.01	6.97
AOX, kg/t	0.0587	0.0185	0.0754	0.0623
% of total AOX	15.0	5.18	17.3	14.7
Cl/C_{100}	2.53	0.94	4.06	2.12