IPST Technical Paper Series Number 540

Correlations Among Contaminant Profiles in Mill Process Streams and Effluents

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November 1994

Submitted to
2nd International Conference on Environmental
Fate and Effects of Bleached Pulp Mill Effluents
November 6–10, 1994
Vancouver, British Columbia, Canada

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Abstract

Two intensive monitoring studies conducted at the Georgia-Pacific facilities at Leaf River, MS and Brunswick GA. showed the absence of TCDD/F, trisubstituted and higher chlorophenols, and acrolein in any of the process sewers. The eighteen sampling episodes conducted at Leaf River allowed correlations to be drawn among the various contaminant profiles. For example, AOX and COD in the final effluent were strongly correlated suggesting that variations in each parameter were governed by process changes.

In 1993/1994, Georgia-Pacific conducted two studies to assess the environmental status of its Leaf River and Brunswick operations. Both of these are ECF (complete ClO_2 substituted) bleach mills. The Leaf River study covered a five week period in August-September 1993, and a four week interval in January-February 1994. The study was designed to capture variability resulting from both seasonal and day-to-day process changes. Process lines were sampled along with the final effluent which led to data on the impact of various unit operations on final effluent quality. The Brunswick effort was shorter and occurred over a three day period in January 1994. A principal finding in both mills was the absence of dioxins, chlorophenols or acrolein in any of the samples taken. Additionally, the large body of data acquired for Leaf River allowed interrelationships to be developed among the concentration-time profiles of the various constituents.

DESCRIPTION OF SITE ACTIVITIES

Leaf River

The Leaf River mill is located in New Augusta, Mississippi. The mill began operations in 1984 and is in the market bleached Kraft sub-category. During the study, daily production approximated 1,500 tons of both hardwood and softwood bleached Kraft market pulp. Approximately 60% of the wood received is softwood and 40% is hardwood. The mill operates a single pulp line that swings between hardwood and softwood. The digester is a continuous Kamyr dual-vessel hydraulic unit.

During this study, the bleaching sequence for both hardwood and softwood consisted of (1) ClO_2 bleaching, (2) extraction with sodium hydroxide reinforced with oxygen and peroxide, (3) ClO_2 bleaching, (4) extraction with sodium hydroxide and peroxide, and (5) final bleaching with ClO_2 (D-Eop-D-E_p-D). Pulp dryer whitewater is used as wash water for the final bleaching (D2) stage, while D2 stage filtrate is used as make up for the E2 washer. Filtrate is normally recycled to the previous stage of the bleach plant all the way back to the first stage.

The nominal kappa number of the pulp entering the bleach plant was 30 for softwood and 14 for hardwood. The pulp is considered elemental chlorine free and is designated as "ECF" in the industry. The kappa factors for softwood and hardwood were at 0.12. Both softwood and hard-

wood are bleached to a final ISO brightness of 90. The chemical recovery plant includes a Kamyr falling film evaporator with a capacity of 1.08 million lb. water per hour, and a Gotaverken recovery boiler rebuilt to handle over 6.0 million pounds of liquor solids per day.

Approximately 20 million gallons of water is taken daily from the Leaf River, treated by coagulation in a clarifier and passed through gravity filters before process use. Only the first and second stage filtrates are sewered; the others are used as wash water in the preceding stage.

The treatment system consists of a bar screen, two primary clarifiers, equalization, cooling, activated sludge treatment in an aeration basin, two secondary clarifiers, and a final holding pond.

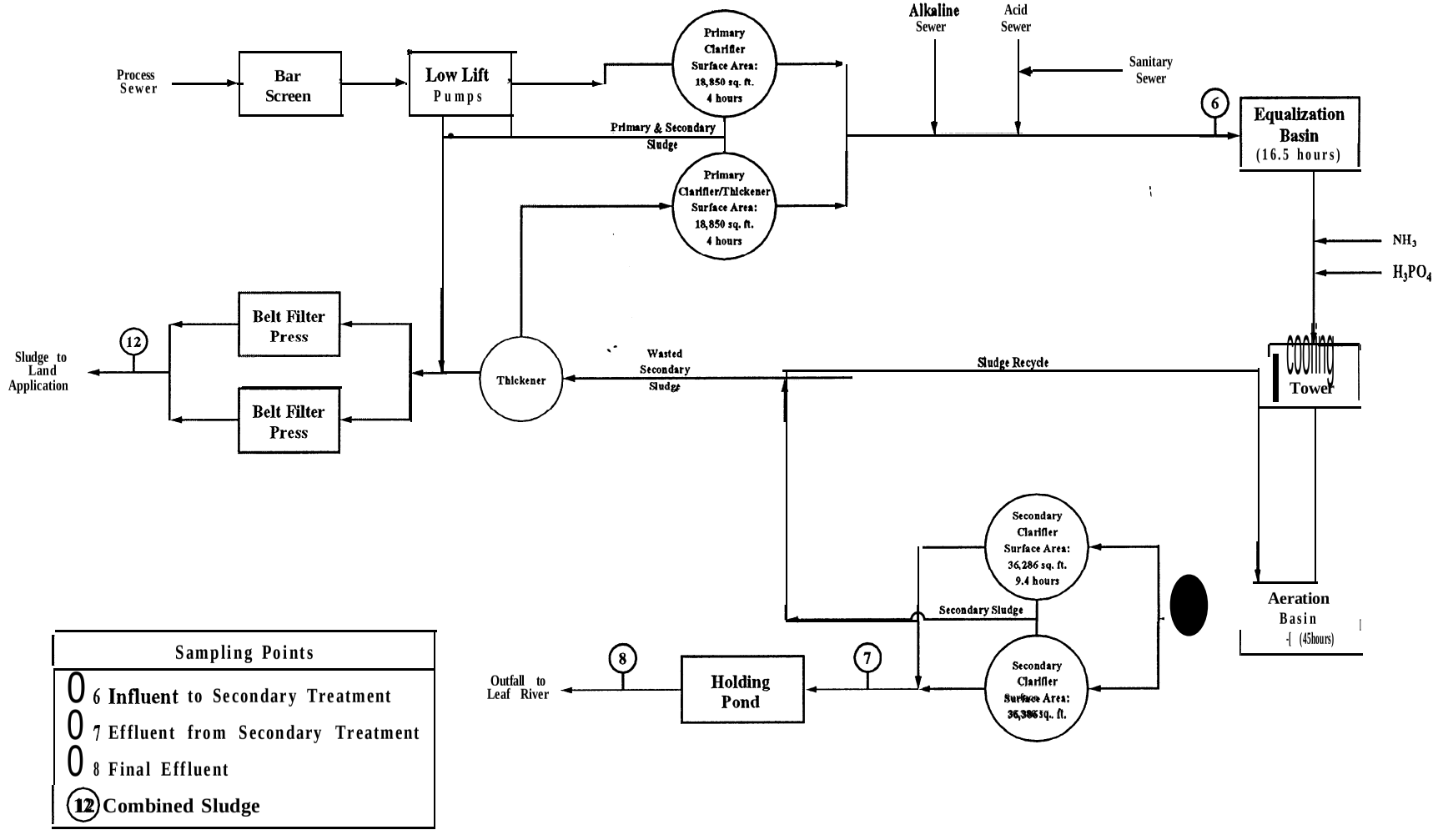
Wastewater from the chemical recovery area, the pulping area, the pulp dryer, the woodyard, and the power boiler, as well as stormwater, enters the wastewater treatment system through the bar screen. The wastewater is then pumped to two 155-foot diameter primary clarifiers in parallel. Detention time in each of the primary clarifiers is four hours. Effluent from the primary clarifiers is discharged to an equalization basin after introduction of the bleach plant acid and alkaline sewers and addition of lime for pH adjustment.

The equalization basin, with ten floating aerators each driven by a 40 HP motor, has a surface area of 237,864 square feet and a detention time of 16.5 hours. Following equalization, nutrients (ammonia and phosphoric acid) are added, and the wastewater flows to a cooling tower which discharges to a 48-million gallon aeration basin. The aeration basin has a detention time of 45 hours and is aerated by four 700-HP aerators. After the aeration basin, the flow is divided between two 215 foot diameter secondary clarifiers, each with a detention time of 9.4 hours. Approximately 8 MGD (40%) of the secondary sludge is recycled to the aeration basin. The secondary clarifiers discharge to a holding pond which discharges continuously through diffusers to the Leaf River. The typical detention time for the holding pond is approximately 60 hours. The mill discharges approximately 18 million gallons per day of treated wastewater to the Leaf River. A schematic for wastewater treatment is provided in Figure 1.

Brunswick

The facility pulps mostly softwood (loblolly and slash pine) and some hardwood (mainly gum, oak, hickory and ash). The mill operates 19 digesters: 11 for softwood, and 8 for both softwood and hardwood. Pulp yields are 11.6 tons per small digester and 17.9 tons per large digester.

Figure 1
Leaf River Wastewater Treatment Schematic



Three bleach lines are run under the following specifications:

	species	production (tph)	
		avg	maximum
No. 1 plant	pine	22	24
No. 2 plant	hwd/pine	32	40
No. 3 plant	pine	36	40
total: 2150 tons/day			

The sequence used is $DE_{op}DE_pD$. Peroxide is used for high brightness EF-100 and for preventing brightness reversion. The towers are all upflow in the No. 2 and No. 3 plants. The No. 1 plant uses both upflow and downflow towers.

The D_{100} stage (for pine) has a retention time of 15-25 min., and is controlled to a CEK-number of 3.5 determined by a correlation of wet brightness to CEK-number. The consistency is 4%, and the temperature is 90-95F. The D_1 stage has a retention time of 1.5 hours and is controlled to 82 Elrepho brightness. The consistency is 11%, and the temperature is 135-145F. The E_{op} stage has a retention time of 30 minutes, an oxygen dosage of 12 lbs/ton, and a peroxide dosage of 2-8 lbs/ton. The extraction stage is peroxide enhanced with 0.75% NaOH. Temperature is 165F, and pH is controlled to a 10.8 target with in-line probes. The D_2 stage is basically the same as the third stage but with 0.4% ClO_2 added and is run at a temperature of 195F.

Washing is counter-current with machine white water (or fresh water) to 5th stage, 5th to 4th stage, 4th to 3rd stage, 3rd to 2nd stage, 2nd to top showers 1st stage, sewer 2nd stage remainder. Fresh water is used on the bottom of the 1st stage showers. Of the 20,000 gallons/ton of total water use, the bleach plant discharges 10,500 gallons/ton.

The recovery boilers used are (i) a Babcox and Wilcox unit installed in 1971 with a capacity of 3.3 M# solids/day, and (ii) a Tampella boiler installed in 1990 capable of processing 4.5 M# solids/day.

Primary treatment occurs in a Dorr-Oliver clarifier operated at a rate of 20-24 million gallons/day. Secondary treatment is conducted in a 6 acre presettling basin (8.6 hr retention), an 88 acre aeration lagoon (5.14 day retention), a 6 acre settling lagoon (8.6 hr. retention). The aeration lagoon has 39 Ashbrook (75 or 100 HP) and two Aire-O_2 100 HP surface aerators. Total flow to the river is 40 mgd. BOD removal is 90,000 lb/day which represents a 90% removal rate. Water is drawn from 8 wells at an average depth of 238 feet. The mill uses 40 mgd of fresh water.

SAMPLING AND ANALYSIS

Leaf River

Samples were taken over a five-week period in August-September 1993 (10 episodes), and a four-week interval in January-February 1994 (8 episodes). Six grab samples were taken over a 24-hour period and composited where appropriate. Every 4 hours the sampler (a) recorded pH, conductivity, and temperature of the sample and also (where necessary) the temperature of the cooled sample from the sampling train, (b) added about 0.5 L to the compositing container and, if required, (c) collected volatile and methanol samples. For samples taken from the chlorination stage, the sampler additionally measured residual chlorine in the sample and added sodium thiosulfate to the first sample added to the compositing container.

The sampling plan is provided in Table 1. Some of the summer analyses were discontinued in the winter event since the analytes were not detected in any of the summer episodes. Since the ACF and ACS locations gave very similar results for all the analytes considered, ACF sampling was discontinued in the winter. Chlorophenols were dropped from the WTI and WTE, and acrolein analysis was discontinued completely, since they were not observed in the summer event. Useful resin acid data could not be obtained for the summer sampling due to analytical difficulties; these were resolved before the winter event.

Chlorophenol analysis was limited to the following congeners: 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,3,4,6-tetrachlorophenol, pentachlorophenol, 3,4,6-tri-chloro-guaiacol, 3,4,5-trichloroguaiacol, 4,5,6-trichloroguaiacol, tetrachloroguaiacol, 3,4,6-trichlorocatechol, 3,4,5-trichlorocatechol, tetrachlorocatechol, trichlorosyringol. Analysis of volatiles was restricted to methylene chloride, acetone, chloroform, 2-butanone and acrolein (summer only).

Brunswick

Samples were taken from the acid and alkaline filtrates from each of the three bleach lines, the acid sewer, the process water intake, the clarifier effluent and the final effluent. The analytes determined at Brunswick were identical to those examined at Leaf River except that DOC, TOC and resin acids were not run.

Analytical Methods

The analytical methods used are listed in Table 2.

Table 1: Sampling plan at Leaf River

	MPW	ACF[1]	ACS	ALF	WTI	PMS	RCS	EVS	WTE	CSI	CSO
color	x	x	x	x	x	x	x	x	x		
pH	x	x	x	x	x	x	x	x	x		
cond.	x	x	x	x	x	x	x	x	x		
TSS	x				x	x	x		x		
COD	x	x	x	x	x	x	x	x	x	x	x
DOC	x	x	x	x	x	x	x	x	x		
TOC	x				x	x	x	x	x		
AOX	x	x	x	x	x				x		
BOD	x				x	x		x	x	x	x
resin acids	x	x	x	x	x	x	x	x	x		
methanol	x	x	x	x	x	x	x	x	x	x	x
chloro-phenols	x	x	x	x	x				x		
volatiles	x	x	x	x	x	x		x	x		
TCDD/F[2]		x		x							

[1]dropped for the winter sampling; [2]episodes 1 and 11 only

MPW: mill process water

ACF: acid filtrate

ACS: acid sewer

ALF: alkaline filtrate

WTI: influent to waste treatment

PMS: pulp mill sewer

RCS: recovery sewer

EVS: evaporator sewer

WTE: waste treatment effluent

CSI: condesate stripper inlet

CSO: condensate stripper outlet

Table 2: Analytical Methods Used		
Analyte	**Method**	**Basis**
methanol	8015A	GC
chlorophenolics	EPA 1653	acetylation, GC-MS
volatiles	624	purge & trap GC-MS
TCDD/F	NCASI 551	HR GC/MS
AOX	1650A	combustion/coulometry
COD	410.4	oxidation/titration
color	NCASI 253	spectrophotometry
BOD	Std. Meth. 507	dissolved O_2 meas.
conductance	EPA 600; 120.1	conductivity
TSS	EPA 160.2	gravimetry
resin acids	NCASI 501	ethylation, GC-FID
TOC	EPA 9060	combustion, CO_2 analysis

RESULTS

Leaf River

The following analytes were not detected at the listed locations in any of the samples taken: chlorophenols (all locations); acrolein (all locations), dichlorodehydroabietic acid (all locations); neoabietic acid (ALF, ACS); 14-chlorodehydroabietic acid (ACS, PMS, RCS, EVS, WTI, WTE); 12-chlorodehydroabietic acid (ACS, PMS, RCS, EVS).

A full scale dioxin analysis was run on ALF and ACF samples taken during episode 1. No 2378-TCDD/F was detected, but OCDD was detected at 0.06 ppt in the ALF sample (detection limit 0.02 ppt). A single 2378-TCDD/F scan was run on the ALF sample taken during episode 11; the analytes were non-detectable.

Brunswick

No chlorophenols or dioxins were found in any of the samples.

Correlations of Contaminant Profiles at Leaf River

Concentration profiles of all the constituents were regressed against one another. Only a few of these relationships will be discussed here to illustrate the utility of the approach; a fuller account will be published later.

Regressions involving COD with $r>0.8$ are presented in Table 3. The COD-TOC relationships are not surprising since they probably reflect similar constituents. The PMS-COD vs PMS-BOD relationships illustrated in Figures 2 and 3, respectively, are interesting since it is the only strong BOD-COD correlation recorded in all the regressions. It appears that the carbon in the

pulp mill sewer (or a fixed fraction thereof) is biodegradable. The PMS contains a substantial amount of resin acids which are biodegradable, although at a slower rate than a smaller compound such as methanol. The pond efficiency at Leaf River was about 98% for resin acids. One conclusion from this relationship is that the PMS-COD will not be a heavy contributor to the COD of the final effluent since much of it will biodegrade. Similar reasoning applies to the evaporator sewer (EVS) BOD-COD relationship.

The WTE-COD and WTE-AOX profiles are illustrated in Figures 4 and 5, respectively. Since the range of COD concentration is much greater than that of AOX, the two constituents are not related directly; rather they must both reflect a common cause. Since end-of-pipe AOX does not biodegrade in the treatment system, it should correlate with other constituents in the process that are also not readily biodegradable such as WTE-COD. Both parameters are, therefore, related to the amount of lignin removed, and the profiles reflect changes in operations such as hard wood/softwood swings. Most of the COD at Leaf River originates from the bleaching process; e.g., half of the COD entering the influent to waste treatment in the first episode originated from the acid and alkaline sewers. This situation reflects a clean well-run mill; presumably, the relationship would not be as good if COD entered the system from sources other than the bleach plant. Based on this limited site-specific data it appears that in the absence of upsets, AOX and COD are surrogates for each other in the final effluent. More importantly, it implies that efforts to reduce COD through treatability will also reduce AOX.

The RCS-COD and RCS-conductivity correlations are somewhat misleading. COD was less than 900 ppm for all but episodes eleven and twelve where it shot up to 32,000 ppm and 100,000 ppm respectively. The conductivity was correspondingly high on these occasions. Clearly, the relationship reflects a spill rather than steady-state situation, and confirms that conductivity is a good way to monitor black liquor spills.

Some correlations were expected but not found. For instance, a relationship between ALF-AOX and ACS-AOX was expected on the grounds that they should both proportionately vary with hardwood/softwood swings and other process variables. Surprisingly, this was not the case as illustrated in Figures 6 and 7. It appears that the AOX split between acid and alkaline filtrates is different for hardwood and softwood. Also, there is much more variability in the ALF-AOX than in the ACF-AOX suggesting that hardwood/softwood differences have a stronger influence on base-extractable AOX.

In summary, we have demonstrated the absence of dioxins, chlorophenols or acrolein in 100% ClO2 bleaching. We have shown the utility of developing relationships among contaminant profiles across various locations and analytes. These correlations will be extended and we expect them to establish source-sink relationships and to provide insight into the transport of these materials through the mill.

Table 3: Relationships between analyte profiles involving COD[1]	
	r
PMS-COD vs PMS-BOD	.997
RCS-COD vs RCS-TOC	.995
RCS-COD vs RCS-TSS	.99
PMS-COD vs PMS-color	.99
RCS-COD vs RCS-conductivity	.98
PMS-COD vs PMS-MEK	.98
RCS-COD vs RCS-color	.96
ALF-COD vs ALF-DOC	.93
WTE-COD vs WTE-color	.92
RCS-COD vs RCS-DOC	.90
WTI-DOC vs ALF-TOC	.88
WTE-COD vs WTI-TSS	.87
WTI-COD vs ALF-DOC	.86
PMS-COD vs RCS-methanol	.85
EVS-COD vs EVS-BOD	.84
EVS-COD vs EVS-conductivity	.84
ALF-COD vs ALF-color	.83
ALF-COD vs ALF-methanol	.82
WTE-COD vs WTE-AOX	.82
WTE-COD vs WTE-TOC	.80
[1]n=18	

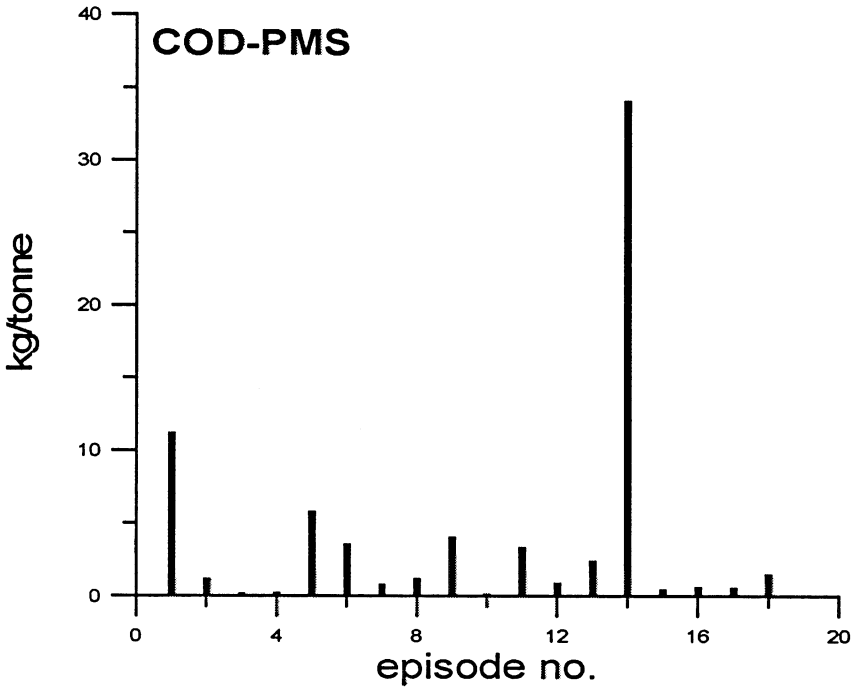


Figure 2 COD profile for the pulp mill sewer

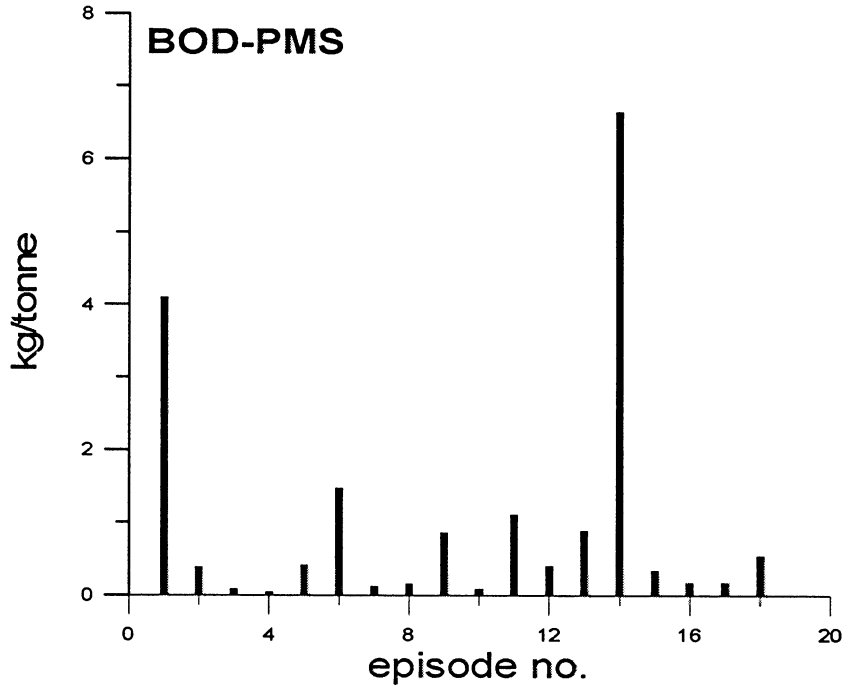


Figure 3 BOD profile for the pulp mill sewer

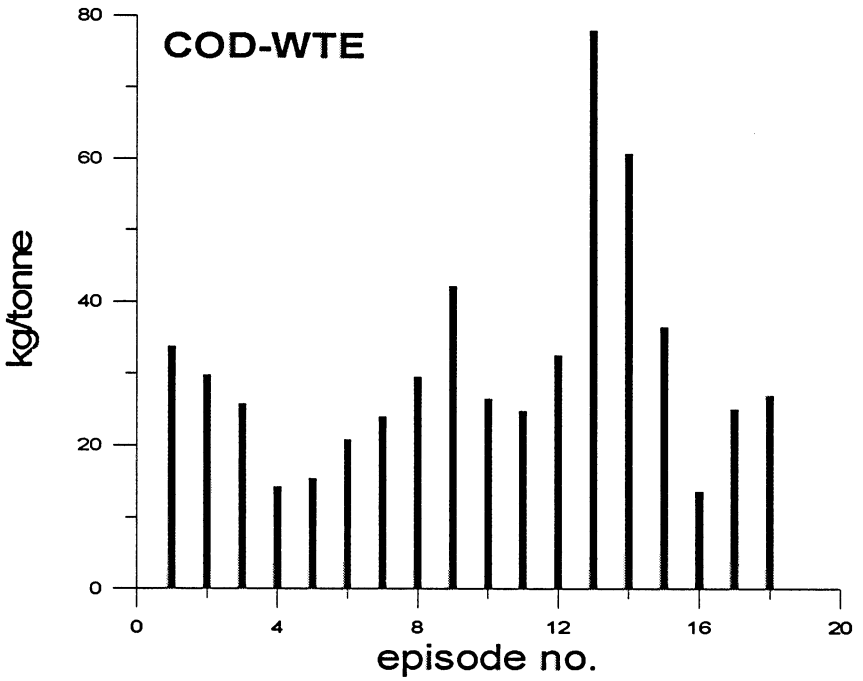


Figure 4 COD profile for the final effluent

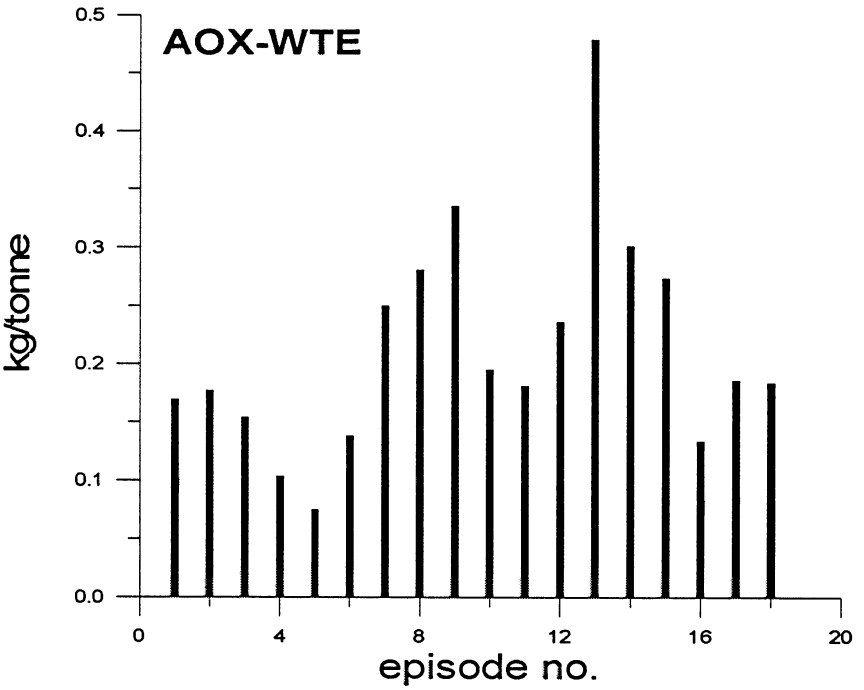


Figure 5 COD profile for the final effluent

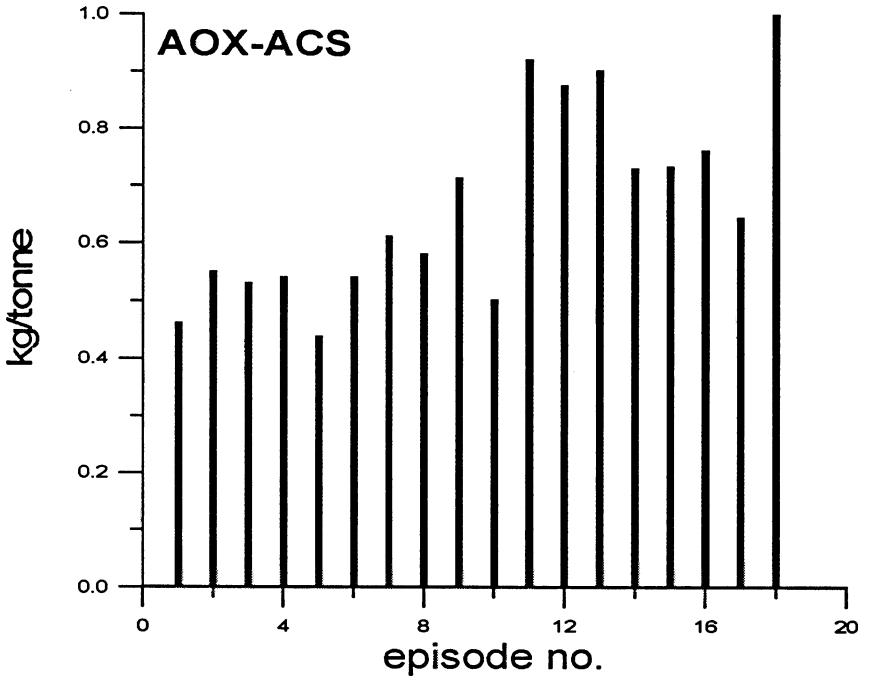


Figure 6 AOX profile for the acid sewer

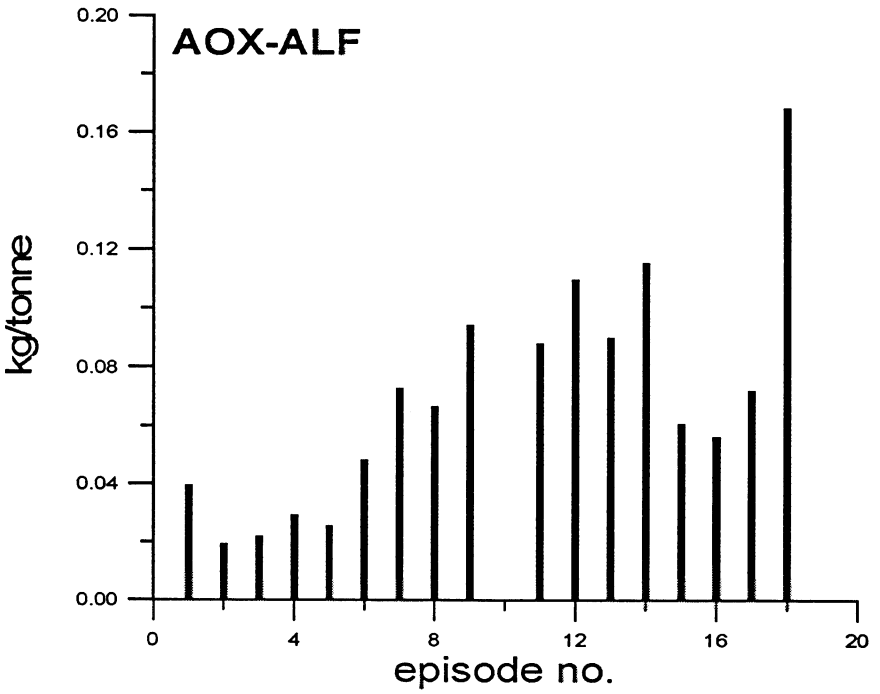


Figure 7 AOX profile for the alkaline sewer