INTERNATIONAL PACIFIC SALMON
FISHERIES COMMISSION

PROGRESS REPORT

No. 25

TOXICITY AND TREATMENT OF DE-INKING WASTES CONTAINING DETERGENTS

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D. W. MARTENS, R. W. GORDON
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NEW WESTMINSTER, B. C.
CANADA
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INTERNATIONAL PACIFIC SALMON
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Appointed under a Convention
Between Canada and the United States for the
Protection, Preservation and Extension of
the Sockeye and Pink Salmon Fisheries
in the Fraser River System

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ABSTRACT

Some lethal and sublethal effects on juvenile sockeye (Oncorhynchus nerka) and pink salmon (O. gorbuscha) of proposed de-inking wastes and the detergents contained therein were investigated. The toxicity of de-inking wastes was attributed primarily to its content of nonionic detergents, Nalco 808 and Sterox MJ-b. These detergents caused lethargy, excessive mucous secretion on the gills and depressed oxygen consumption of salmon fry at concentrations less than the lethal level. The biochemical oxygen demand (BOD) of de-inking wastes was easily reduced by biological treatment, as reported elsewhere, but the wastes were generally not readily detoxified owing to resistance of the detergents to detoxification. Detergents were removed from solution by activated carbon but this method of treatment would be costly since pre-treatment to remove excess organic matter and suspended solids would be required. Thus the alternatives for treatment of the proposed wastes appeared to be selection of detergents which would be readily detoxified during biological treatment, or selection of a method such as activated carbon treatment which was capable of removing the detergents.

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TOXICITY AND TREATMENT OF DE-INKING WASTES CONTAINING DETERGENTS

INTRODUCTION

Industrial development on the Fraser River watershed is constantly increasing and untreated waste discharges pose a significant hazard to fish life. Recently, an existing mill which utilizes waste paper for remanufacture into paperboard and building paper proposed adding a de-inking mill to its operation. De-inking is essentially a laundry process (Casey, 1952) and detergents are required in order to produce a suitable quality finished product. Unfortunately, detergents are known fish toxicants and their presence in de-inking waste could constitute a hazard to juvenile and adult salmon migrating in the Fraser River. Thus the International Pacific Salmon Fisheries Commission, in fulfilling its responsibility for protection of Fraser River sockeye (Oncorhynchus nerka) and pink salmon (O. gorbuscha), undertook a study of the toxicity and treatment of the proposed waste effluents.[1]

The proposed new mill in the lower Fraser watershed will de-ink both ledger and newsprint paper for remanufacture into new paper products. Since chemical requirements for de-inking these two types of paper differ, they would be processed separately, but not simultaneously, resulting in discharge of two different wastes. In addition, the existing mill will continue producing paperboard (and some building paper), resulting in discharge of a third effluent (hereafter termed paperboard waste) in combination with either of the former two.

The de-inking process consists of (1) loosening and defibering the stock and (2) washing ink from the fibers using detergents which are subsequently discharged with the mill waste. Thus the waste contains fibers and organic matter derived from the ink and paper, as well as detergents. Although chemical requirements for de-inking ledger paper and newsprint differ somewhat, effluents from processing both types of paper were expected to contain similar amounts of the same two proprietary nonionic detergents, Nalco 808 and Sterox MJ-b.

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[1] This study was financed by the Governments of Canada and the United States with a part of the United States contribution originating from the Federal Water Quality Administration of the U.S. Department of the Interior.

De-inking wastes have been reported amenable to biological treatment. Biochemical oxygen demand (BOD) was reduced 82% by primary clarification followed by biological oxidation (Palladino, 1952). In another case, BOD of de-inking wastes was reduced 74% by 4 days of biological oxidation in an aerated lagoon (Blosser, 1961). However, in neither case were measurements made to determine whether the detergent content or toxicity to fish was reduced by treatment. Since some detergents are resistant to biological oxidation and could remain unchanged, toxicity to fish might persist in biologically treated de-inking wastes.

As the study reported herein progressed, studies elsewhere (Canada Dept. Fisheries and Forestry, personal communication) showed that in-plant changes in chemical usage would adequately detoxify the paperboard waste from the existing mill. For economic reasons it was then considered desirable to detoxify de-inking wastes by some treatment method prior to mixing with paperboard waste for discharge. Consequently, the major part of the study was concentrated on de-inking wastes, although some data concerning mixtures of de-inking and paperboard waste are included since these studies were completed before the in-plant changes were developed.

Thus the first objective of this study was to measure toxicity to juvenile salmon of de-inking wastes and of the detergents contained therein; the second objective was to evaluate biological and activated carbon methods of waste treatment to reduce toxicity.

MATERIALS AND METHODS

De-inking wastes were produced in a pilot plant at the mill site and were transported to Cultus Lake laboratory where all studies were conducted. Owing to limited operation of the pilot plant it was necessary to store accumulated wastes in a cool room (38°F) at the laboratory, for up to 3 weeks before testing. On two occasions de-inking wastes and paperboard wastes were mixed at the mill in the ratio of 1 to 5 in order to duplicate the wastes expected following mill expansion. Thus five waste mixtures were studied and are designated as follows: ledger, newsprint, paperboard (pb), ledger-paperboard (ledger-pb) and newsprint-paperboard (newsprint-pb). Samples of the two nonionic detergents

used in the de-inking process, Nalco 808 (Alchem Ltd.) and Sterox MJ-b (Monsanto), were supplied through courtesy of the Canada Department of Fisheries and Forestry.

The acute toxicity of wastes and detergents to juvenile salmon was measured in bioassays and the sublethal effects of detergents on oxygen consumption were determined. Toxicity reduction by biological oxidation and activated carbon treatment was then evaluated.

Chemical and Physical Tests of Wastes

The 5-day biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids and pH of each shipment of wastes were measured upon arrival at the laboratory. Biochemical oxygen demand was measured by the dilution method (Standard Methods, 1965). Chemical oxygen demand was measured by the modified dichromate method (Dobbs and Williams, 1963). Suspended solids were determined using glass mats in Gooch crucibles. A Beckman Model G pH meter was used to measure pH.

Bioassays of Wastes and Detergents

Bioassays were used to measure initial toxicity of raw wastes and detergents, and were also used to evaluate the effectiveness of biological treatment methods. The bioassays used to measure the acute toxicity of raw wastes and detergents were conducted by exposing 10 young salmon, either sockeye fingerlings, sockeye fry or pink salmon fry, to a series of dilutions made with Cultus Lake water for 96 hr at about 48 to 50°F. Fingerlings and fry were bioassayed in 23-liter and 1-liter aquaria, respectively. Aquaria were aerated with aquarium air pumps. Mortalities in each dilution after 96-hr exposure were used to calculate the 96-hr median tolerance limit (96-hr TL_m) which is the waste concentration (per cent by volume or ppm detergent) at which half the number of fish would survive the test (Standard Methods, 1965). Bioassays of treated wastes and detergents (treatment described later) were carried out for 96 hr at a single high concentration, usually in the range of 50 to 90% concentration (90 parts treated waste, 10 parts Cultus Lake water) to evaluate toxicity reduction attained by treatment. The limited volume of treated

material available precluded the series of solutions necessary to calculate a 96-hr TL_m.

Sockeye fry were of the Cultus Lake or Pitt Lake races and had been reared 30 days in the laboratory to a wet weight of 0.25 to 0.35 gm when bioassays commenced. Sockeye fingerlings were from Cultus Lake stock reared 10 months in the laboratory to a weight of about 8.5 gm. Pink salmon fry were of Sweltzer Creek stock captured from an artificial spawning ground at the laboratory and were bioassayed within 1 to 2 days following emergence when their weight was around 0.25 gm. All fish were in excellent condition and mortalities were nil among control groups during bioassays. Fish were not fed for 24 hr prior to or during bioassays.

Test of Sublethal Effects of Detergents

The sublethal effects of de-inking detergents were determined by measuring and comparing oxygen consumption rates of sockeye salmon fry exposed to various dilutions of detergents. Oxygen consumption measurements were conducted in a water bath at 46.5 to 47°F which equaled the temperature at which the fish were being reared in the laboratory.

The tests were conducted using five sockeye fry averaging about 0.5 gm wet weight in each of a series of 525-ml glass-stoppered bottles containing a known concentration of detergent (experimental) or lake water only (control). Bottles were filled with water drawn from an air-saturated 5-gal reservoir. Fish were added to control and experimental bottles, these were carefully stoppered and sealed to exclude bubbles and were placed on their sides in darkness of a covered constant-temperature water bath.

After the 3- to 5-hr test period, which was accurate to within ± 10 sec for each bottle in a particular test, water was siphoned from each bottle into a 300-ml BOD bottle and dissolved oxygen was measured by the Azide modification of the Winkler method (Standard Methods, 1965). Comparison of dissolved oxygen in blank controls (no fish) at the end of the test with dissolved oxygen in the reservoir at the start indicated no change in oxygen concentration had occurred. Oxygen levels typically exceeded 11 ppm at the start of a test and declined to a minimum of 4.6 ppm in one case (TABLE 1), but usually remained above 5 ppm. As shown in the example in TABLE 1, the difference between

dissolved oxygen in blanks and that in controls or experimental bottles was the amount of oxygen used by the fish. Oxygen consumption rate was calculated as milligrams of oxygen utilized per hour per gram of dry weight of fry. Relative oxygen consumption rate is expressed as the ratio of respiration rate of experimental to control fish.

TABLE 1 - Example of results from oxygen consumption rate test.

Test Bottle	No. Fish	Elapsed Time min	Dissolved Oxygen		Mean Dry Weight of Fish mg	Oxygen Consumption Rate	
			Measured mg/l	Used mg/l		Absolute mg/hr/gm	Relative
Blank	0	251	11.40	-	-	-	-
Control	5	237	4.81	6.59	66.31	2.004	1.000
Control	5	236	5.27	6.13	66.38	2.457	
Experimental (7.5 ppm Nalco 808)	5	234	4.63	6.77	103.17	1.768	0.792

Upon completion of each experiment, fish were preserved in 10% formalin, dried at 98°C for 24 hr and weighed individually on an analytical balance accurate to 0.01 mg. In order to eliminate behavior as a factor in measuring oxygen uptake, several tests were performed using fish which had been anesthesized with 1:3500 2-phenoxyethanal. This concentration has been suggested as effectively anesthetizing 9- to 11-inch pink salmon (Bell, 1964) and proved satisfactory for sockeye fry used in these tests. Following each test in which anesthesia was employed, fish were revived and behavior was observed for a few minutes to determine if they appeared normal.

Biological Treatment of Wastes and Detergents

Generally, the harmful effects of organic wastes can be reduced by biological treatment, i.e. by subjecting the waste to intense bacterial activity. Under suitable conditions, bacteria may break down the active materials in the wastes into simpler and generally less active compounds. In order to test a biological method of waste treatment, a bacterial culture or "activated sludge" is developed on the waste, acclimated to degrading the

organic compounds present, then tested in fresh loads of waste to determine treatment effectiveness.

De-inking Wastes

Heterogeneous microbial cultures (activated sludges) were grown in 9-liter aerobic treatment units on each of the two de-inking wastes and on a mixture of ledger-pb waste. Cultures were started by seeding the wastes with domestic sewage and soil elutriate and were maintained each day by refilling with fresh waste after supernatant was decanted following 1 hr of settling. Although nitrogen and phosphorous may have been present in the wastes, these inorganic nutrients were added at the rate of 200/10/1 (applied BOD/N/P), using ammonium chloride and dipotassium hydrogen phosphate.

After activated sludges had been grown on wastes for a minimum of 6 days, treatment effectiveness was evaluated on fresh loads of waste, after treatment periods ranging from 24 to 216 hr, using measurements of toxicity, BOD and COD. Foam was controlled by addition of a drop of Dow Corning Anti-Foam B, which control bioassays showed was nontoxic to salmon in amounts greater than those used herein.

De-inking Detergents

Activated sludges were initially acclimated separately to Nalco 808 and Sterox MJ-b detergents while growing on synthetic sewage (Soap and Detergent Assoc., 1966). Acclimation was necessary since detergents are not readily degradable; separate acclimation was used to ensure that each detergent was being degraded. Following 2 weeks of acclimation, as recommended by the Soap and Detergent Association (1966), the activated sludges were combined and maintained on a daily ration consisting of 42 ppm Nalco 808 and 14 ppm Sterox MJ-b plus 60 ml synthetic sewage stock solution (TABLE 2) to make a total volume of 9 liters.

TABLE 2 - Synthetic sewage stock solution (Soap and Detergent Association, 1966).

Glucose	13.0 gm
Nutrient broth	13.0
Beef extract	13.0
Dipotassium hydrogen phosphate	13.0
Ammonium sulfate	2.5
Tap water to make 1 liter	

Following approximately 4 months on the combined ration, trials were conducted to determine whether toxicity of the detergent solutions could be eliminated by biological oxidation. This 4-month period was not necessary for acclimation but suited the convenience of the laboratory. Activated sludge was settled and 200 ml of the sludge was added to each of a series of five treatment units containing either small amounts of synthetic sewage stock solution, inorganic nutrients, or neither of these. Volumes were made up to 9 liters with tap water and detergent to give concentrations of 42 ppm Nalco 808 and 14 ppm Sterox MJ-b. At intervals of 24, 48, 120 and 168 hr, aliquots were removed, filtered through glass wool to remove the activated sludge and bioassayed at 65% concentration to determine if toxicity had been reduced or removed. As in the previous tests, foam was controlled by adding a drop of Dow Corning Anti-Foam B.

Activated Carbon Treatment of Detergents

The effectiveness of activated carbon as a means of removing Nalco 808 and Sterox MJ-b from solution was evaluated using Filtrasorb 300 (Calgon Corp.) packed in a glass tube 4.5 ft long by 0.5 inch I.D. Solutions of detergent in distilled water, either 40 ppm Nalco 808 or a mixture of 42 ppm Nalco 808 and 14 ppm Sterox MJ-b, flowed into the top of the column by gravity from a 60-liter reservoir kept nearly full during a run. Flow rate was maintained at 44.2 ml/min, equivalent to 10.4 U.S. gpm/ft^2 of carbon. Sampling ports were located 1.5, 3 and 4.5 ft from the top of the column, and water samples were collected periodically from each port to estimate detergent concentration.

Since Nalco 808 and Sterox MJ-b are nonionic detergents their concentration could not be measured by the methylene blue test commonly employed for anionic detergents. As a substitute, an indirect method of analysis was developed, based upon the foaming characteristics of the surfactants in distilled water. Comparisons were made in the range of 0 to 5 ppm for Nalco 808 and 0 to 4 ppm for Sterox MJ-b with the known comparator solutions arranged in increments of 0.5 ppm. Thus unknown concentrations greater than 5 ppm Nalco 808 or 4 ppm Sterox MJ-b were diluted until foam characteristics indicated surfactant concentration was within the test range. When solutions of sufficient concentration to form a distinct foam layer ($>$ 2.5 ppm Nalco 808; $>$ 3.5 ppm

Sterox MJ-b) were compared, criteria such as thickness of the foam layers and times required for the foam layers to break were considered in determining if the unknown surfactant concentration was greater or less than that of the known comparator. When solutions which did not form a distinct foam layer were compared ($<$2.5 ppm Nalco 808; $<$3.5 ppm Sterox MJ-b), the thickness of the rings of foam formed against the inside walls of the test tubes and appearance of solutions following agitation were considered in determining relative concentrations. Estimated accuracy of this method of analysis is reported in TABLE 3.

TABLE 3 - Estimated accuracy of the foam test used to measure detergent concentration.

Detergent Concentration mg/l	Accuracy mg/l
0 - 2.5	± 0.25
2.6 - 5.0	± 0.50
5.1 - 10.0	± 1.0
10.1 - 25.0	± 2.5

The foam test method of detergent analysis did not differentiate between Nalco 808 and Sterox MJ-b and when these were used in combination, comparator solutions were made with Nalco 808. Tests showed the accuracy of measuring the combined total of detergents using Nalco 808 as a reference was equal to those in TABLE 3.

RESULTS

Chemical and Physical Characteristics of Wastes

The BOD and COD of ledger waste, approximately 400 and 1,200 ppm respectively, were much higher than corresponding values for newsprint or paperboard waste or mixtures of the de-inking and paperboard waste (TABLE 4). Mixtures were in the ratio 5 parts paperboard waste to 1 part de-inking waste. With the exception of one sample of newsprint waste, suspended solids were lower in de-inking wastes than in paperboard waste or mixtures of the two.

TABLE 4 - Characteristics of de-inking and paperboard (pb) wastes.

Waste	Load No.	BOD ppm	COD ppm	Suspended Solids ppm	pH
Ledger	1	422	1,192	50.0	9.8
	2	398	-	12.9	10.4
Newsprint	1	108	553	18.0	7.7
	2	88	-	17.2	7.4
	3	120	-	228.0	6.1
Paperboard (pb)	1	127	146	241.0	6.2
Ledger-pb	1	155	427	224.0	9.8
	2	-	214	-	5.6
Newsprint-pb	1	108	411	168.0	6.2
	2	-	-	106.0	5.7

The pH of ledger wastes was near 10 while pH of newsprint waste approached neutrality, averaging 7.0 for the three samples tested. Paperboard waste was slightly acidic but when mixed with ledger waste at the mill the pH ranged from 5.6 to 9.8 indicating that the individual wastes had different alkalinities (TABLE 4).

Mild agitation was sufficient to create significant amounts of foam on de-inking wastes, whereas paperboard waste was less inclined to foam owing to the low concentration of detergent used in processing. The high concentration of detergents reportedly in the de-inking wastes undoubtedly accounted for the difference.

De-inking wastes studied by Palladino (1952) and Blosser (1961) were generally higher in BOD and suspended solids than those reported herein, with the exception of ledger waste which was similar in BOD. Palladino reported BOD in the range 445 to 510 ppm and suspended solids over 2,000 ppm; Blosser reported BOD's ranging from 172 to 505 ppm and suspended solids of 639 ppm. Differences in waste strength may be related to differences in processing and raw paper supplied.

Toxicity of Wastes

Ledger and newsprint de-inking wastes were much more toxic than paperboard waste, probably owing to the high content of toxic detergents used in the de-inking process (TABLE 5). Mixtures of ledger-pb and newsprint-pb wastes were of intermediate toxicity owing to dilution of de-inking waste by the less toxic paperboard waste. Although small amounts of detergent (Rexol J25) were used in the paperboard process, toxicity of the waste was related to sizing resin and slimicides (Canada Dept. Fisheries and Forestry, personal communication). The bioassays involving paperboard waste shown here were conducted prior to in-plant changes in sizing resin and slimicides which adequately detoxified the waste and therefore are not considered representative of discharges following these alterations.

TABLE 5 - Acute toxicity of de-inking and paperboard wastes to sockeye salmon fry, except where noted.

Waste	Load No.	Toxicity 96-hr TL_m % Waste by Volume
Ledger	1	3[a]
	2	7[b]
Newsprint	1	5[a]
	2	9, 11[b]
	3	20
Paperboard (pb)	1	43[a]
Ledger-pb	1	23[a]
	2	37
Newsprint-pb	1	34[a]
	2	42

[a] sockeye salmon fingerlings
[b] pink salmon fry

Loads of the same process waste were not of identical toxicity which is to be expected when dealing with an industrial effluent (TABLE 5). It is believed that foam produced during aeration did not significantly reduce toxicity. However, in each case the first load was most toxic, and later

inquiries indicated the company was testing lower detergent concentrations in subsequent pilot plant trials of the de-inking process. In addition, the fact that the second loads of ledger-pb and newsprint-pb were less toxic than the first may have resulted from slight detoxification during a 3-week storage period before the second loads could be bioassayed. Considering the foregoing variables, the fact that sockeye fingerlings were the test species used to bioassay initial loads of waste does not mean that they were necessarily less tolerant than sockeye or pink fry used in bioassays of later loads. This subject was not explored further since the quantity of waste available from the pilot plant was limited (the remainder being required for detoxification tests), thus precluding studies of differences in tolerance between salmon species or age groups. However, in one instance both sockeye and pink fry bioassayed using newsprint waste were about equally susceptible. Thus data obtained using sockeye fry are considered generally applicable to pink salmon, although further testing would be required to confirm this conclusion.

The gills of dead fish taken from bioassays of de-inking waste and mixtures of de-inking and paperboard waste were generally coated with mucous, which probably played a role in death of the fish by blocking oxygen transfer. Mucous was sometimes seen on fish which survived bioassays. Gills of fish used in bioassays of paperboard waste alone were not examined. On the other hand, the greatest mucous concentrations were associated with bioassays of de-inking wastes alone, implicating detergents as the cause of excessive mucous secretion.

The behavior of fish during bioassays was observed through transparent bioassay chambers. Fish showed no outward symptoms of distress during initial exposure to de-inking waste concentrations which later proved lethal. However, at such waste concentrations fish generally showed distress in a few hours, lost equilibrium within 24 hr and sank passively to the bottom where death followed shortly thereafter. The criterion of death was absence of an opercular beat and in some cases fish were lethargic to such an extent that this was the only sign of life noted. Thus, although not dead, such fish were unable to function normally.

Toxicity of Detergents

Acute Toxicity

Nalco 808 and Sterox MJ-b were highly toxic to sockeye fry, the latter being slightly more toxic (TABLE 6). Mucous secretions similar to those found on fish during bioassays of de-inking wastes were found on gills of fish during bioassays of detergents. The behavior of fry was similar to that noted for de-inking wastes with lethargy a common occurrence even at 6 ppm Nalco and 4 ppm Sterox where mortalities were nil. It is evident that nonlethal but harmful effects noted with de-inking wastes are associated with exposure to detergents.

Using 96-hr TL_m data and assuming Nalco 808 and Sterox MJ-b have similar toxic action, it can be calculated that when these detergents are present at 42 and 14 ppm, respectively, the waste should have a 96-hr TL_m of about 12%. Since actual 96-hr TL_m's were generally lower (TABLE 6), indicating a more toxic waste, it is possible that either or both of the detergents may have exceeded predicted concentration levels, thereby accounting for greater toxicity. It is also possible that other toxic substances were present or that the two detergents combined were more toxic than when tested separately. Unfortunately there is no way of determining whether one or a combination of these factors was contributing to added toxicity.

TABLE 6 - Acute toxicity of detergents to sockeye salmon fry.

Detergent	Concentration ppm	Survival %	Time hr	96-hr TL_m ppm
Nalco 808	9	0	72	7.7
	8	40	96	
	7	80	96	
	6	100	96	
Sterox MJ-b	7	0	48	5.5
	6	30	96	
	5	70	96	
	4	100	96	

Effect on Oxygen Consumption

Detergents caused a decrease in oxygen consumption rate of sockeye fry which was dependent on detergent concentration (FIGURE 1). Oxygen consumption rate ranged from about 80% of normal at the 96-hr TL_m concentration to about 93% at 13% of the 96-hr TL_m. Reduced oxygen consumption was apparently not associated with behavior since results were similar whether or not fish were anesthetized. Such a result suggests detergents were having a direct effect upon oxygen transfer mechanisms of the gills. This was evidently the case at lethal concentrations of detergent since excessive mucous noted during bioassays probably restricted flow of water over the gills, thereby reducing oxygen consumption. The secretion of mucous indicates that sensitive gill tissues were irritated, and oxygen consumption data show that this irritation was great enough at sublethal concentrations to reduce oxygen transfer efficiency to less than normal.

Treatment of Wastes and Detergents

Biological Oxidation

Reductions in BOD of de-inking wastes ranged from 19 to 98% and were generally greater at longer aeration times and higher concentrations of biological suspended solids (i.e. activated sludge) (TABLE 7). From a BOD reduction standpoint, satisfactory treatment could be expected in treatment units such as aerated lagoons, as reported earlier (Blosser, 1961).

Toxicity reductions accompanied biological oxidation but in no case was the waste completely detoxified, that is, permitting 100% survival of fish in undiluted treated waste. Reductions in toxicity were significant for the second load of ledger de-inking waste where survival was 100% in a 90% treated waste concentration (90 parts treated waste plus 10 parts water) following 72 hr of treatment. On the other hand, the first load of ledger de-inking waste was toxic at only 19% concentration following 24 hr of treatment. Newsprint de-inking waste was not readily detoxified since survival was only 40 to 60% at treated waste concentrations in the range of 50 to 80%. Neither prolonged aeration, up to 168 hr, nor increased suspended biological solids concentration significantly influenced detoxification of any of the three loads of newsprint de-inking waste. The presence of mucous on gills of dead fish in

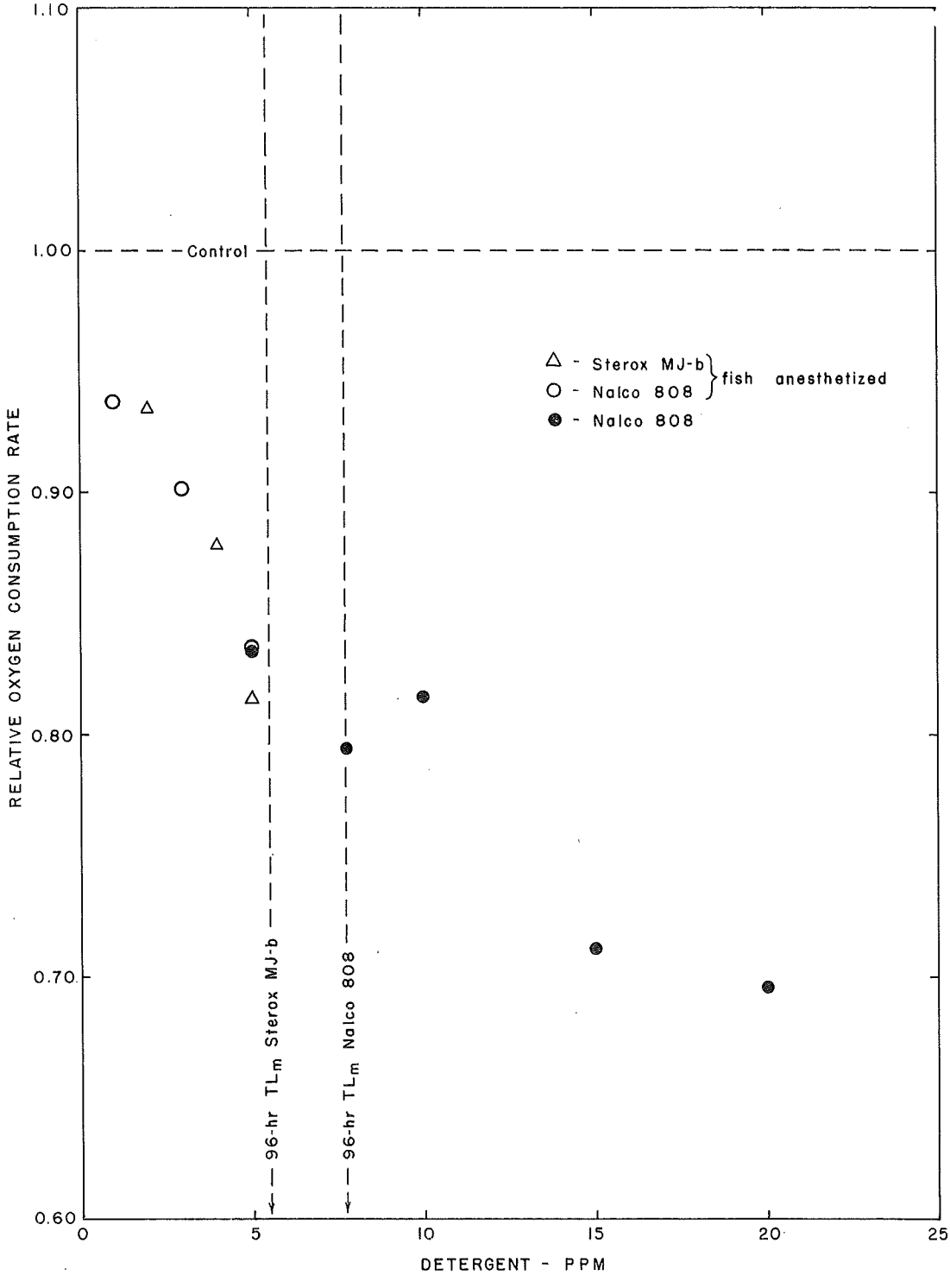

FIGURE 1 - Effect of detergents on oxygen consumption rate of sockeye salmon fry.

TABLE 7 - Effect of biological treatment of ledger and newsprint de-inking wastes on BOD and toxicity to sockeye fry, except as noted.

Waste Type and Load	Initial BOD ppm	BOD Reduction %	Aeration Period hr	Biological Suspended Solids ppm	96-hr TL_m Before Treatment: Waste Concentration %	96-hr Survival in Various Concentrations of Treated Waste: Concentration %	Survival %
Ledger De-inking							
1	422	28	24	206	3[a]	19	50[b]
2	398	74	24	600	7[b]	80	0[b]
	↓	84	48	333	↓	90	80[b]
		92	72	423		90	100[b]
		98	216	197		90	100[b]
Newsprint De-inking							
1	108	54	24	574	5[a]	30	0[a]
2	88	19	24	45	9, 11[b]	80	40
	↓	65	24	105	↓	45	50
		41	48	53		80	0
		76	72	62		80	40
		65	96	44		80	60
		94	144	21		80	40
	↓	95	168	31	↓	80	60
3	120		72		20	60	40
	↓		96		↓	65	20
			120			65	60
		>75	24	256		40	90
	↓	>95	72	251		60	50
	240[c]	>75	24	428		50	50
	240[c]	>95	24	428	↓	55	50

[a] sockeye salmon fingerlings

[b] pink salmon fry

[c] dextrose added equivalent to 120 ppm BOD

bioassays suggested that detergents were responsible for mortalities.

The greater toxicity reduction of the second load of ledger de-inking waste compared with the other four leads of de-inking waste cannot be explained. Since ledger de-inking waste had a much higher initial BOD, this source of additional energy might have assisted in more complete oxidation of detergents. However, addition of dextrose equal to 120 ppm BOD to newsprint waste (load 3) did not result in additional detoxification even though BOD reduction exceeded 95%. Possibly a longer aeration period or addition of a greater BOD was necessary to obtain further toxicity reduction. Although of interest, this point was not explored further since addition of extra BOD was believed impractical at this industrial site. Differences in toxicity reduction may have been related to different detoxification rates and concentrations of Nalco 808 and Sterox MJ-b. If one of these nonionic detergents was more readily detoxified than the other and happened to predominate in the second load of ledger de-inking waste, this might account for the greater toxicity reduction attained. Finally, as mentioned earlier, toxic substances besides detergents may have been present and not removed by treatment.

The possibility that detergents were resistant to detoxification was pursued using activated sludge following a 4-month growth period on 42 ppm Nalco 808 and 14 ppm Sterox MJ-b. A test of detoxification was conducted using aeration periods from 24 to 168 hr. The detergent mixture remained toxic following 24 and 48 hr of treatment but was detoxified after 120 hr of biological treatment (TABLE 8). The presence or lack of synthetic sewage or nitrogen or phosphorous had no apparent affect on detoxification. Nutrient reserves normally stored by activated sludge were probably utilized during treatment in those cases where they were not supplied.

The results are similar to those obtained with de-inking wastes, except that one load of ledger de-inking waste was essentially detoxified within 72 hr. However, as mentioned previously, the concentration of detergent in the de-inking wastes was not precisely known, making comparison speculative. In any case, it is evident that the de-inking wastes and detergents studied herein require extensive treatment to remove toxicity.

TABLE 8 - Effect of biological treatment on toxicity of detergent mixture (42 ppm Nalco 808 plus 14 ppm Sterox MJ-b) to sockeye fry.

Aeration Period hr	Synthetic Sewage Added ml	Biological Suspended Solids ppm	% Survival at 65% Concentration Treated Detergent Mixture
24	5.0	97	0
	1.0	167	0
	0.0[a]	158	0
	0.0	150	0
48	5.0	182	0
	1.0	175	0
	0.0	175	0
120	3.0	240	100
	1.0	190	100
	0.0[a]	250	100
	0.0	348	100
168	1.0	42	80
	0.0[a]	140	100
	0.0	135	100

[a] K_2HPO_4 and NH_4SO_4 added equivalent to amount in 1.0 ml synthetic sewage.

Activated Carbon

Activated carbon effectively removed Nalco 808 and Sterox MJ-b from solution (FIGURE 2). Detergent increased in the effluent as greater volumes were treated, reaching levels equivalent to the 96-hr TL_m of Sterox MJ-b when about 200 liters had passed through a 4.5-ft column. In order to produce a nonlethal effluent, detergent concentration should definitely not exceed 4 ppm which means the volume treated in a 4.5-ft column may reach 120 liters, equivalent to a carbon dosage of 4.9 lb carbon per 1,000 U.S. gal. Thus detergent concentration in treated effluent would range from 0 to 4 ppm as adsorptive capacity of a carbon column was utilized. Since treatment cost is related to the amount of carbon required, low carbon dosages are desirable and there are good indications that the foregoing dosage could be lowered. Tests to remove ABS detergent (an anionic non-biodegradable detergent) using activated carbon showed that at a flow of 10 U.S. gpm/ft^2, a threefold increase in column length decreased carbon loading by a factor of 2.7 (Joyce and Sukenik, 1964). Since the flow rate used herein was also 10 U.S. gpm/ft^2, and assuming carbon has similar adsorptive capacities for ABS, Nalco 808 and Sterox MJ-b detergents, increasing column length from 4.5 to 13.5 ft would decrease carbon loading from 4.9 to 1.8 lb per 1,000 U.S. gal. The foregoing authors suggest further economy can be realized by operating several short columns and renewing individual columns countercurrently when effluent quality falls to a specified level.

DISCUSSION

Toxicity of Wastes

Changes in chemical usage in the paperboard process during conduct of this study adequately detoxified the paperboard waste (Canada Dept. Fisheries and Forestry, personal communication), therefore only de-inking wastes from a proposed plant require consideration. At time of this writing the proposed de-inking plant has been held in abeyance for economic reasons.

Both the proposed ledger and newsprint de-inking wastes were highly toxic to juvenile sockeye and pink salmon and were, by comparison, more toxic than kraft pulp mill bleach plant wastes (Servizi, Gordon and Stone, 1966). The major toxic components of de-inking wastes were two nonionic detergents,

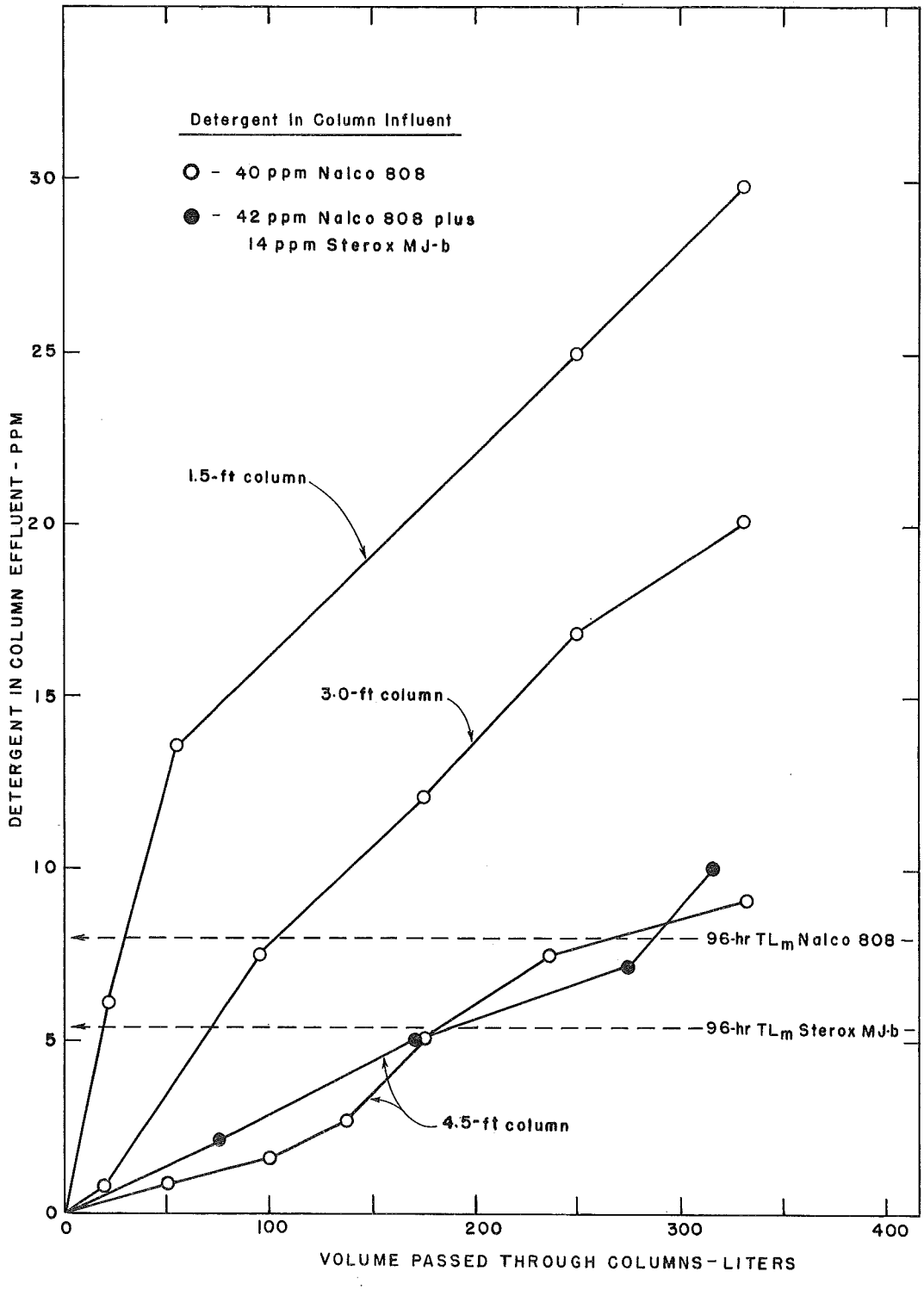

FIGURE 2 - Adsorption of Nalco 808 and Sterox MJ-b detergents by activated carbon columns.

Nalco 808 and Sterox MJ-b, which designers of the de-inking mill believed would occur in the wastes at 42 and 14 ppm, respectively. These concentrations exceeded levels acutely toxic to sockeye salmon fry by approximately 6 and 3 times, respectively, and far exceeded concentrations at which sublethal toxic effects were noted. Although they may not be directly responsible for death of fish, sublethal toxic concentrations impose added stresses which reduce the likelihood that a fish will survive in a competitive environment geared to elimination of weaker individuals through predation, disease and a limited food supply.

Three types of sublethal toxic effects were noted. First, observations made during bioassays showed that fish were lethargic at detergent concentrations which were nontoxic during 96-hr bioassays. Second, excessive mucous secretions were noted on gills. Third, studies using sockeye salmon fry not previously exposed to detergents revealed that Nalco 808 and Sterox MJ-b depressed oxygen consumption below normal rates at concentrations which were less than 20% of the toxic level.

Prolonged exposure to detergents might have depressed oxygen consumption further since studies elsewhere have shown that gills and other sensitive tissues are very susceptible to irreversible damage by detergents at low concentrations. Twenty-four-hour exposure of pumpkinseed sunfish, Lepomis gibbosus (Linnaeus), to 18 ppm ABS (an anionic non-biodegradable detergent) resulted in gill damage which was irreversible in 8 weeks in detergent-free water (Scheier and Cairns, 1966). Yellow bullheads, Ictalurus natalis (LeSueur), suffered erosion of taste buds and impairment of swimming and feeding behavior following exposure to ABS and LAS (an anionic biodegradable detergent) at concentrations of only 0.5 ppm (Bardach, Fujiya and Holl, 1965). Affected fish did not fully recover after 6 weeks in detergent-free water. It is noteworthy that the yellow bullhead is considered tolerant of pollution. Exposure of rainbow trout (Salmo gairdneri Richardson) to 5 ppm ABS detergent resulted in erosion of gill epithelium and fusion of respiratory folds which diminished oxygen consumption and was followed by death from suffocation (Schmidt and Mann, 1961). These authors speculated that salt imbalance might occur as well, since gills play a role in this function. This latter point is of considerable importance since salmon are required to maintain physiological

salt balances while migrating between fresh and salt water. Any impairment of osmoregulatory ability would seriously affect ability of salmon to make the transitions necessary to complete their life cycle.

Results of this study and those cited above show that considerable hazard to fish is associated with discharge of detergents. Owing to the high toxicity of de-inking wastes and the potential hazard posed by detergents contained therein, it is recommended that treatment be used to detoxify these wastes prior to discharge.

Waste Treatment

Biological oxidation, in forms such as activated sludge and aerated lagoons, has found considerable application in the treatment of industrial wastes, including de-inking wastes. However, treatment success has generally been measured in terms of BOD reduction with little attention paid to detoxification. The results reported herein show that although BOD reduction was considerable, de-inking wastes were generally not adequately detoxified during biological treatment. Further testing indicated that nonionic detergents in the de-inking waste were only slowly detoxified even after 4 months growth of activated sludge on the detergents in question.

Thus if biological treatment were selected as the method to detoxify de-inking wastes, detention times of several days would be required, with careful attention paid to developing and maintaining a culture acclimated to detergent detoxification. Difficulty might be experienced in maintaining an acclimated culture since it was proposed that the de-inking process would shut down between runs. This deficiency might be overcome by adding paperboard waste plus a small amount of Nalco 808 and Sterox MJ-b to the treatment unit on days when de-inking waste was not available.

The resistance of detergents to biological oxidation is not peculiar to those in de-inking wastes. Many detergents, notably the ABS type, are not removed in municipal sewage treatment plants and thus have been the subject of considerable research (Bogan and Sawyer, 1955; McKinney and Symons, 1959). Biodegradable detergents of the LAS type were subsequently developed to alleviate the serious pollution problems associated with non-biodegradable detergents (Tarring, 1964). Consideration should be given to a similar kind

of substitution in the case of de-inking waste since a more easily degradable detergent would make biological waste treatment more likely to succeed.

Nalco 808 and Sterox MJ-b were readily removed from solution by activated carbon. Although detergents remaining in solution reached 4 ppm, the maximum nonlethal level, at a dosage of 4.9 lb carbon per 1,000 U.S. gal of mixture treated, calculations indicated dosages of 1.8 lb per 1,000 U.S. gal might be feasible with further reductions possible by manipulating flow rate and using a series of short columns. The latter dosage is moderate by waste treatment standards.

These dosages were based upon removing only detergents from solution, but de-inking wastes contain additional organic matter which would use carbon capacity unless removed beforehand. In addition, removal of suspended materials must form part of the pre-treatment sequence in order to prevent plugging of the carbon column. Thus chemical flocculation might be required as a pre-treatment method to insure adequate carbon life. It is evident from the above discussion that use of activated carbon as a treatment method is likely to cost much more than biological oxidation. However, if change to readily degradable detergents in the de-inking process is not practical, then activated carbon treatment has the greatest chance of being not only a successful but also a dependable treatment method.

Thus the alternatives for detoxification of de-inking wastes appear to be selection of detergents which are readily biodegradable during biological treatment or selection of a treatment method such as activated carbon which is capable of removing the detergents presently proposed.

CONCLUSIONS

1. The proposed de-inking wastes are highly toxic to sockeye and pink salmon fry and should be detoxified prior to discharge. Toxicity is associated primarily with nonionic detergents which irritate and damage sensitive tissues such as gill epithelia.

2. The detergents in the proposed de-inking waste cause sublethal toxic effects in salmon consisting of lethargy, excessive mucous secretion and depressed oxygen consumption at nonlethal concentrations.

3. Biological treatment is effective in reducing BOD of the proposed de-inking wastes but detoxification is not readily accomplished owing to resistance of the detergents to detoxification. However, if the detergents are replaced by some which are readily detoxified, biological treatment could prove efficient and dependable.

4. Detergents presently proposed for use in de-inking are readily removed from solution by activated carbon but the presence of additional suspended and soluble organic matter in de-inking waste makes this type of detoxification dependent upon pre-treatment to remove excess organics.

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