INTERNATIONAL PACIFIC SALMON FISHERIES COMMISSION

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

PROGRESS REPORT

No. 32

DECHLORINATION OF MUNICIPAL SEWAGE USING SULFUR DIOXIDE

BY

D. W. MARTENS and J. A. SERVIZI

NEW WESTMINSTER, B. C.
CANADA
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ABSTRACT

Simultaneous continuous flow bioassays of primary treated, chlorinated and dechlorinated municipal sewage were conducted with sockeye and pink salmon to evaluate the effectiveness of sulfur dioxide on removal of chlorine and chlorine induced toxicity.

Chlorination decreased the average Mean Survival Time (MST) of sockeye in undiluted primary treated sewage from 293 minutes to 32 minutes. Dechlorination increased the average MST to 434 minutes indicating that all the chlorine induced toxicity and some primary sewage toxicity was removed. However, sewage which had received primary treatment remained acutely toxic to sockeye and pink salmon following chlorination-dechlorination.

Dissolved oxygen and pH were not adversely affected by sulfur dioxide. The cost of dechlorination using sulfur dioxide is discussed. Lagooning is recommended as an alternative to chemical dechlorination where flows are small and land requirements not great.

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INTRODUCTION

Toxicity of primary treated and chlorinated sewage at Lulu Island Sewage Treatment Plant (STP) was the subject of a previous investigation (Martens and Servizi, 1974). Evidence of the acutely toxic nature of primary treated municipal sewage[1] corroborated with an earlier field investigation (Servizi and Martens, 1974) and with work of other investigators (Esvelt, Kaufman and Selleck, 1973; Zillich, 1972). A previous study at Lulu Island S.T.P. indicated that acceptable disinfection[2] could not be obtained by chlorination without substantially increasing toxicity of primary sewage to sockeye salmon fingerlings (Oncorhynchus nerka) (Martens and Servizi, 1974). Based upon experience of others (Esvelt, Kaufman and Selleck, 1973; Zillich, 1972) it was recommended that chemical dechlorination using sulfur dioxide be tested as a means of eliminating chlorine residual and chlorine induced toxicity.

Free chlorine and chloramine residuals are destroyed by sulfur dioxide as positive chlorine atoms are reduced to negative chloride atoms as described in the equations below. The reaction is reported to proceed nearly instantaneously (White, 1972). The stoichiometric relationship requires 0.9 mg/l SO_2 to dechlorinate 1 mg/l free or combined chlorine residual.

Free chlorine

$$SO_2 + HOCl + H_2O \longrightarrow SO_4^{=} + Cl^{-} + 3H^{+} \qquad (1)$$

Dichloramine

$$2SO_2 + NHCl_2 + 4H_2O \longrightarrow 2SO_4^{=} + 2Cl^{-} + 5H^{+} + NH_4^{+} \qquad (2)$$

Monochloramine

$$SO_2 + NH_2Cl + 2H_2O \longrightarrow SO_4^{=} + Cl^{-} + 2H^{+} + NH_4^{+} \qquad (3)$$

1 The terms "primary sewage", "chlorinated sewage" and "dechlorinated sewage" will be used to describe sewage which has been "primary treated", "primary treated and chlorinated for disinfection" and primary treated chlorinated for disinfection and dechlorinated with sulfur dioxide respectively.

2 Acceptable disinfection was defined as a median Most Probable Number of coliform bacteria per 100 mls of sewage (MPN) less than 10,000.

Sulfur dioxide reacts with dissolved oxygen as described below and raises the possibility that reaeration may be required to maintain dissolved oxygen levels in the effluent as specified by regulatory agencies.

$$2SO_2 + 2H_2O + O_2 \longrightarrow 2H_2SO_4 \quad (4)$$

Furthermore, the reaction of sulfur dioxide with chlorine and dissolved oxygen forms acids which might affect pH of dechlorinated sewage if buffering capacity is unsufficient.

A full-scale system to dechlorinate effluent at the Lulu Island primary sewage treatment plant using sulfur dioxide was installed by Greater Vancouver Sewerage and Drainage District and became operational in February 1974. Thereafter commenced a cooperative study including Greater Vancouver Sewerage and Drainage District, Canada Department of Environment (Fisheries Service and Environmental Protection Service) and the International Pacific Salmon Fisheries Commission to evaluate this facility. The effect of dechlorination on MPN of coliforms, pH, dissolved oxygen and acute toxicity to sockeye salmon fingerlings and pink salmon alevins (O. gorbuscha) was assessed during the study.

METHODS

Bioassay Site

The Lulu Island sewage treatment plant employed prechlorination for odor control, preaeration, settling and chlorination in its initial design. Dechlorination using sulfur dioxide was added to the downstream portion of the chlorine contact chamber. The chlorine contact chamber was a rectangular channel with a theoretical average detention time of 60 minutes to the point of sulfur dioxide injection during the study. Compound-loop chlorination was used to maintain a constant residual to the point of sulfur dioxide addition. Chlorine residual was recorded by an automatic amperometric analyzer 10 ft upstream of sulfur dioxide injection. Sulfur dioxide was injected at the entrance to a constriction in the channel added to direct flow past a 25 hp turbomixer used to disperse sulfur dioxide in the sewage. The dosage of sulfur dioxide required to dechlorinate was controlled on a flow proportional basis. There were approximately 15 minutes detention between sulfur dioxide addition and the effluent weir leading to the discharge pipeline and the Fraser River.

Residual sulfur dioxide and chlorine were measured in grab samples collected at the effluent weir.

During the previous study a portion of the sewage entering the Lulu Island treatment plant was effluent from an activated sludge plant. During the study reported herein the activated sludge plant was no longer on line, thus influent consisted of raw municipal sewage. An electroplating plant discharged 100,000 Igpd of wastes to the municipal sewer system following limited pretreatment. Mean sewage flow through the Lulu Island treatment plant during the study was 2.92 x 10^6 Igpd.

Bioassays

Simultaneous continuous flow bioassays were conducted using primary, chlorinated and dechlorinated sewage to provide comparative toxicity data. Acclimation of test fish to dilution water pumped from the Fraser River was intended to be a minimum of seven days. However, owing to failures in the dilution water pump, this was not achieved in every case (TABLE 1). Sockeye and pink salmon were reared from eggs at Sweltzer Creek Laboratory. Sockeye eggs were obtained from Pitt Lake and Cultus Lake races, while pink salmon eggs were from the Sweltzer Creek race. Bioassays were conducted in 30 liter glass aquaria with flow rates creating a 99% replacement rate in about 2.8 hours (Sprague, 1973). Ten sockeye fingerlings (mean wet weight 2.91 gms) and in some bioassays ten sockeye fingerlings and ten pink salmon fry (mean wet weight 0.15 gms) were exposed up to 96 hours in sewage, sewage-water mixtures and in control (dilution) water. Pink salmon were held in nylon screened cages (4 in. diameter x 2½ in. long) separated from sockeye which occupied the main body of the aquarium. The total daily inflow to aquariums averaged about 38 liters per gram of fish per day, well in excess of the recommended value of two to three liters per gram of fish per day (Sprague, 1972).

The chlorinated sewage and dechlorinated sewage dilution apparatuses each contained six concentrations while the primary sewage dilution apparatus contained five concentrations plus the dilution water control. To facilitate comparison, bioassays of primary, chlorinated and dechlorinated sewage were started at intervals comparable to elapsed time in the chlorination and dechlorination processes.

TABLE 1 - Acclimation of fish to Fraser River dilution water.

Bioassay Number	Acclimation, Days	
	Sockeye	Pink
1	6	-
2	8	-
3	7	-
4	9	-
5	14	-
6	14	-
7	16	-
8	7	-
9	7	7
10	0	0
11	0	0
12	2	2
13	0	0

Sewage and dilution water were supplied to each aquarium from head troughs by precalibrated metering pipettes. Flows from the pipettes were checked at the outset of each bioassay and pipettes were cleaned daily. Test temperatures varied from 4°C (39°F) to 14°C (57°F) during the bioassay period and temperature uniformity in bioassays was maintained by immersing aquaria in a cooling water bath. Dissolved oxygen (D.O.) was maintained with compressed oxygen.

Aquaria were checked almost continuously for mortalities or moribund fish during the initial 8 to 12 hours of each bioassay. Observation of the test fish was restricted by opaqueness of sewage. Thus a net was used to move test fish near the surface for inspection. Mean Survival Time (MST) of test fish was obtained from a graph on logarithmic probit paper of survival time in minutes versus accumulated percent mortality.

Analyses of Sewage and Dilution Water

Dissolved oxygen was measured routinely in each aquarium by the alkali-iodide-azide modification of the Winkler method (Standard Methods, 1971). Temperature, total residual chlorine and sulfur dioxide were also routinely measured in aquaria. Total residual chlorine was measured by the back-titration iodometric method with an amperometric end point (Standard Methods, 1971). The minimum detectable concentration was 0.02 mg/l. Sulfur dioxide measurement was adapted from American Society for Testing Materials (1972) by Greater Vancouver Sewerage and Drainage District and employed amperometric back-titration similar to the amperometric chlorine residual determination. Iodine in excess of the blank (0.0 mg/l chlorine) was calculated as negative chlorine and equated to sulfur dioxide residual. Accuracy and detection limit were the same as those for chlorine residual (± 0.02 mg/l and 0.02 mg/l respectively).

Daily (24 hour) composite sewage samples were analyzed for hardness, alkalinity, pH, Methylene Blue Active Substance (MBAS) and ammonia nitrogen. Hardness and alkalinity were measured by procedures described in Standard Methods (1971). MBAS was measured with a HACH KIT and ammonia nitrogen was measured by the method of Harwood and Kühn (1970). Un-ionized ammonia concentrations were calculated after Trussell (1972).

Sub-samples from the aforementioned daily composite samples were submitted to the West Vancouver Laboratory, Department of the Environment, for atomic absorption spectoprotometric measurement of total extractable (ext) and dissolved (diss) metals (cadmium, calcium, copper, chromium, iron, lead, magnesium, manganese and zinc). Samples for extractable metals were acidified with 5 mls conc. HNO_3/l while samples for dissolved metals were first filtered (0.45) and then acidified with 5 mls conc. HNO_3/l. Further sub-samples were submitted for nitrite, anionic surfactant and cyanide measurements. Nitrite was determined by an automated procedure (Kamphake, Hannah and Cohen, 1967) of the diazotization method described in Standard Methods (1971). Anionic surfactants were measured by the Azure A method (Van Stevenick and Riemersma, 1966) and cyanide (CN^-) was determined after the procedure described in Standard Methods (1971).

Dilution water was analyzed for alkalinity, hardness, chloride, pH, MBAS, ammonia nitrogen and chlorine.

Lulu Island STP staff made daily measurements of chlorides, pH, D.O., Biochemical Oxygen Demand (BOD), chlorine residual, sulfur dioxide residual, MPN and other sewage characteristics pertinent to plant operation.

Decay of Residual Chlorine

Removal of residual chlorine by lagooning may be an alternative to chemical dechlorination where space is available. Since the decay rate of residual chlorine determines detention time required for dechlorination in a lagoon, a test was conducted to measure elapsed time to disappearance of chlorine in the absence of sulfur dioxide. Aerated and not aerated 30 liter volumes of chlorinated sewage in glass aquaria were tested for chlorine residual. Sewage used in the tests was characterized by analyses for MBAS, ammonia nitrogen, chlorides, total alkalinity, EDTA hardness, suspended solids, temperature, D.O. and pH.

RESULTS

Characteristics of Dilution Water and Primary Sewage

Dilution water temperature averaged 8.3°C during the study and varied from 3.9°C to 13.9°C (TABLE 2). Chlorine was not detected and ammonia nitrogen averaged 0.09 mg/l. Chlorides averaged 1,449 mg/l and varied with tide level and wind direction during the day owing to the estuarine location of the intake pumping station. A combination of high tide and strong onshore wind caused the highest chloride content measured in dilution water (3,700 mg/l).

Characteristics of sewage at Lulu Island STP were quite similar to those of the previous study (Martens and Servizi, 1974) with the exception of surfactants which were more typical of municipal sewage (Esvelt, Kaufman and Selleck, 1973) than during the previous study (TABLE 2). The reason for low surfactant concentration during the past study is not known but is believed related to decomposition during storage of samples. Cyanide and nitrite were not measured during the previous study but during the study reported herein were usually present at readily measurable concentrations, averaging 0.11 and 0.04 mg/l, respectively (TABLE 2). Measurement of both total extractable (ext) and dissolved (diss) metals revealed that most of the metal content existed in the dissolved state while the remainder was probably in a colloidal or particulate state. The range in metal content noted in the earlier study persisted and was believed related in part to effluent from an electroplating plant.

TABLE 2 – Dechlorinated sewage and dilution water characteristics.[abc]

Characteristic (mg/l except pH and temp.)	Sewage Mean	Sewage Range		Dilution Water Mean	Dilution Water Range	
Chloride[c]				1,449.	N.D.	3,700
Hardness as $CaCO_3$[c]	65.8	44.0	78.0	369.	45.0	1,200
Alkalinity as $CaCO_3$[c]	117.	107.	130.	50.8	39.5	59.2
pH[c]	7.0[d]	7.0	7.3	7.33	7.30	7.35
Anionic Surfactants	4.47	2.2	8.8			
MBAS[c]	4.7	3.0	6.0	N.D.	N.D.	N.D.
Ammonia Nitrogen[c]	20.34	12.25	23.50	0.09	0.020	0.13[illegible]
Un-ionized Ammonia[c]	0.06	0.03	0.08	0.00	0.00	0.01
Temperature °C [c]	11.1	7.8	13.9	8.3	3.9	13.9
Cyanide CN^-	0.11	0.03	0.36			
Nitrite Nitrogen	0.04	0.005	0.08			
BOD[b]	131.	80.	163.			
Chlorine[c]				N.D.	N.D.	N.D.
Cadmium (ext/diss)	> .01/ .01	<.01/<.01	.04/ .02			
Calcium (ext/diss)	14.1 / –	5.2 / –	16/ –			
Copper (ext/diss)	.16/ .14	.12/ .08	.19/ .19			
Chromium (ext/diss)	.18/ .05	<.1 /<.02	.26/ .10			
Iron (ext/diss)	3.40/1.27	.99/ .17	4.2 /2.3			
Lead (ext/diss)	.05/ .02	<.02/<.02	.13/<.02			
Magnesium (ext/diss)	7.37/ –	4.1 /	11.0 / –			
Manganese (ext/diss)	.23/ .13	.14/ .07	.34/ .19			
Zinc (ext/diss)	.22/ .17	.08/ .07	.80/ .26			

[a] Data courtesy of the Department of the Environment, except as noted.

[b] GVSDD

[c] IPSFC

[d] Mode

Disinfection and Dechlorination

Chlorine was not detected in primary sewage although raw sewage was prechlorinated to control odors. Mean chlorine dosage for disinfection purposes was 10.7 mg/l yielding a residual of about 2 mg/l immediately upstream of sulfur dioxide injection (TABLE 3). Sulfur dioxide dosage and residual averaged about 5.1 and 0.79 mg/l, respectively. Chlorine residual was not detected in 102 of 106 samples following dechlorination but the maximum measured was 1.22 mg/l.

TABLE 3 - Chlorine and sulfur dioxide dosages and residuals, mg/l.[a]

	Mean	Range
DOSAGE		
Chlorine	10.7	5.2 - 16.6
Sulfur dioxide	5.1	1.3 - 14.4
CHLORINE RESIDUAL		
Upstream of Dechlorination	2.0	1.1 - 3.7
Effluent Weir	0.02	0 - 1.22[b]
SULFUR DIOXIDE RESIDUAL		
Effluent Weir	0.79	0 - 3.10

[a] Data courtesy GVSDD.

[b] 96.2% of samples were zero.

Disinfection was measured by the GVSDD using MPN of coliforms at the effluent weir. The median MPN was 1,900/100 ml when chlorine residual was in the range 2.0 to 2.5 mg/l preferred for operation (TABLE 4). The target value was 10,000/100 ml and this level was attained in 105 of 111 samples.

TABLE 4 - Coliform content of disinfected sewage.[a]

Amperometric Chlorine Residual,[b] mg/l	MPN Coliforms/100 mls	
	Median	Range
0 - 1	16,150	2,300,000 - 9,300
1.1 - 1.9	2,300	230,000 - 430
2.0 - 2.5	1,900	4,300 - 230
2.5	1,615	4,300 - 230

[a] Data courtesy GVSDD.
[b] Upstream of Dechlorination.

The effect of dechlorination using sulfur dioxide on pH and dissolved oxygen was measured. The pH of effluent leaving the treatment plant was near neutrality whether or not sulfur dioxide was applied (TABLE 5). However, mean D.O. was 4.5 mg/l when sulfur dioxide was applied and the turbomixer was not operating, indicating no discernible effect on D.O. by sulfur dioxide during contact in the dechlorination chamber. When sulfur dioxide was applied and the turbomixer operated, mean D.O. was 5.2 mg/l and it was presumed that the turbomixer served the dual purpose of rapid dispersion of sulfur dioxide and aeration.

TABLE 5 - Effect of SO_2 on pH and dissolved oxygen.[a]

	pH		Dissolved Oxygen mg/l	
	In	Out	In	Out
Without Dechlorination	7.1	6.8	0.1	4.4
With Dechlorination and Turbomixing	7.2	6.9	0.2	5.2
With Dechlorination but No Turbomixing	7.2	6.8	0.1	4.5

[a] Data courtesy GVSDD.

Chlorine residuals in aquaria containing undiluted, chlorinated sewage averaged 1.35 mg/l (TABLE 6). This value was less than the residual in the chlorine contact chamber owing to exertion of chlorine demand as sewage was distributed to dilution apparatus and bioassay aquaria. In all but undiluted sewage, chlorine residuals ranged upward from less than 0.02 mg/l, however, mean values were commensurate with dilutions.

Residual sulfur dioxide in aquaria containing undiluted dechlorinated sewage averaged 0.83 mg/l (TABLE 6). This value was similar to that measured at the effluent weir, however, sulfur dioxide residual varied over a wide range in aquaria and at the effluent weir.

Average sulfur dioxide residuals in dilutions of dechlorinated sewage exceeded values expected based upon dilution. This result is believed associated with the wide range of sulfur dioxide residuals which occurred in undiluted, dechlorinated sewage.

TABLE 6 - Chlorine and SO_2 residuals in bioassay aquaria.

Type and Percent Sewage in Aquaria	No. Measurements	Residual, mg/l	
		Chlorine	
Chlorinated		Mean	Range
100	20	1.35	0.51-2.12
40	23	0.54	0.02-1.10
17	40	0.21	0.02-0.45
10	51	0.09	0.02-0.18
5	70	0.02[a]	0.02-0.08
2	72	0.02[a]	0.02-0.06
Dechlorinated		Sulfur Dioxide	
100	47	0.83	0.09-2.30
65	15	0.87	0.36-1.58
40	21	0.53	0.22-1.05
25	33	0.31	0.12-0.62
17	35	0.21	0.02-0.42
10	33	0.12	0.02-0.29

[a] Mode

Acute Toxicity

Primary sewage at Lulu Island was usually lethal to juvenile sockeye in 96 hours at 25% v/v and some mortalities occurred at 17% v/v. No mortalities occurred at 10% v/v. The 96 hour LC50 for sockeye was in the range 17 to 25% v/v in four bioassays, between 25 and 40% v/v in another, between 10 and 25% v/v in a sixth and between 10 and 17% v/v in a seventh. The average MST of sockeye fingerlings in primary sewage was 293 minutes (TABLE 7). Pink salmon were included in five bioassays and MST's averaged 346 minutes in undiluted primary sewage. The average MST of sockeye fingerlings during the same bioassays was 158 minutes.

Pink salmon were included in two bioassays of diluted primary sewage. In one, mortalities of pink salmon occurred at 25% v/v, but in the other all survived.

Chlorination caused a substantial increase in toxicity as seen by MST's which decreased to 32 minutes for sockeye (TABLE 7).

TABLE 7 - Acute toxicity of sewage to sockeye fingerlings and pink salmon fry.

Sewage and Species	Mean Survival Time, min. Average	Range	No. Tests	Lowest Concentration Causing Mortality, % v/v	No. Tests
Primary:					
Sockeye	293	110 - 480	13	17	7
Pink	346	272 - 440	5	25	2
Chlorinated:					
Sockeye	32	11 - 98	13	5	7
Pink	27	21 - 37	5	10	2
Dechlorinated:					
Sockeye	434	172 - 620	13	17	7
Pink	728	395 - 1501	5	40	2

The 96 hour LC50 for sockeye was between 5 and 10% v/v chlorinated sewage in four bioassays and between 2 and 5% v/v in the remaining three. Mortalities occurred at 5% v/v but not at 2% v/v chlorinated sewage. The average MST for pink salmon decreased to 27 minutes in five bioassays of undiluted chlorinated sewage while the MST's for sockeye during the same bioassays averaged 19 minutes.

Pink salmon were exposed to a series of dilutions of chlorinated sewage in two bioassays and the 96 hour LC50's were between 5 and 10% v/v. No mortalities occurred among pink salmon at 5% v/v chlorinated sewage in these two bioassays.

Chlorine induced toxicity was removed by dechlorination, consequently the average MST for sockeye fingerlings increased to 434 minutes and the lowest concentration causing mortality was 17% (TABLE 7). The 96 hour LC50 of dechlorinated sewage was between 25 and 40% v/v in two bioassays, between 17 and 25% v/v in three and between 10 and 17% v/v in another. Similarly, the average MST for pink salmon fry increased to 728 minutes and the minimum concentration causing mortality was 40% v/v. The 96 hour LC50 of dechlorinated sewage to pink salmon fry was between 25 and 40% v/v in one case and 40% v/v in another.

The possibility that chlorination-dechlorination removed more than chlorine induced acute toxicity was examined by statistical comparison of MST's for primary and dechlorinated sewage. Significant differences were noted for exposure of both sockeye ($p = 0.02$) and pink salmon ($p = 0.05$). However, the result is of limited practical significance since the lowest concentration at which mortalities occurred was 17% v/v in both effluents (TABLE 7).

Sulfur dioxide was usually present in excess in dechlorinated sewage and averaged 0.03 mg/l during bioassays with the range of measurements from 0.09 to 2.30 mg/l (TABLE 6). A bioassay was conducted in which sockeye fingerlings were exposed to a mean of 2.20 mg/l SO_2 in dechlorinated sewage and the MST was 505 minutes whereas MST of primary sewage during the same bioassay was 480 minutes. This result followed the trend wherein dechlorinated sewage was less toxic than primary.

Decay of Residual Chlorine

Since lagooning may be a suitable method of dechlorination in some cases, decay of chlorine residual in the absence of sulfur dioxide was measured in one test.

Chlorine residual in unaerated and aerated chlorinated sewage declined rapidly during the first three or four hours losing approximately 75% of the initial residual (FIGURE 1). Chlorine residuals which were initially 1.2 mg/l and 1.1 mg/l in unaerated and aerated samples declined to 0.02 mg/l and less than 0.02 mg/l, respectively, in approximately thirteen hours. Initial chlorine residuals in the test were 55 to 60% of the mean (2 mg/l) upstream of dechlorination. If initial residuals had been greater, elapsed time to disappearance of chlorine residual may have exceeded 13 hours. Aeration did not appear to influence elapsed time for dissipation of chlorine residual.

Comparison of characteristics of sewage used during chlorine decay measurements (TABLE 8) with average characteristics (TABLE 2) indicates sewage was representative for the characteristics measured.

TABLE 8 - Characteristics of sewage and dilution water in chlorine decay measurements.

Characteristic[a]	Sewage	Dilution Water
Hardness as $CaCO_3$	72	336
Alkalinity as $CaCO_3$	120	54
pH	7.0	7.3
MBAS	6.8	0.0
Ammonia Nitrogen	22.3	0.09
Temperature °C (°F)	11.1 (52)	11.7 (53)
Dissolved Oxygen	7.8	10.2
Chloride	80	925
BOD	147	1.05

[a] - mg/l, except pH and temperature.

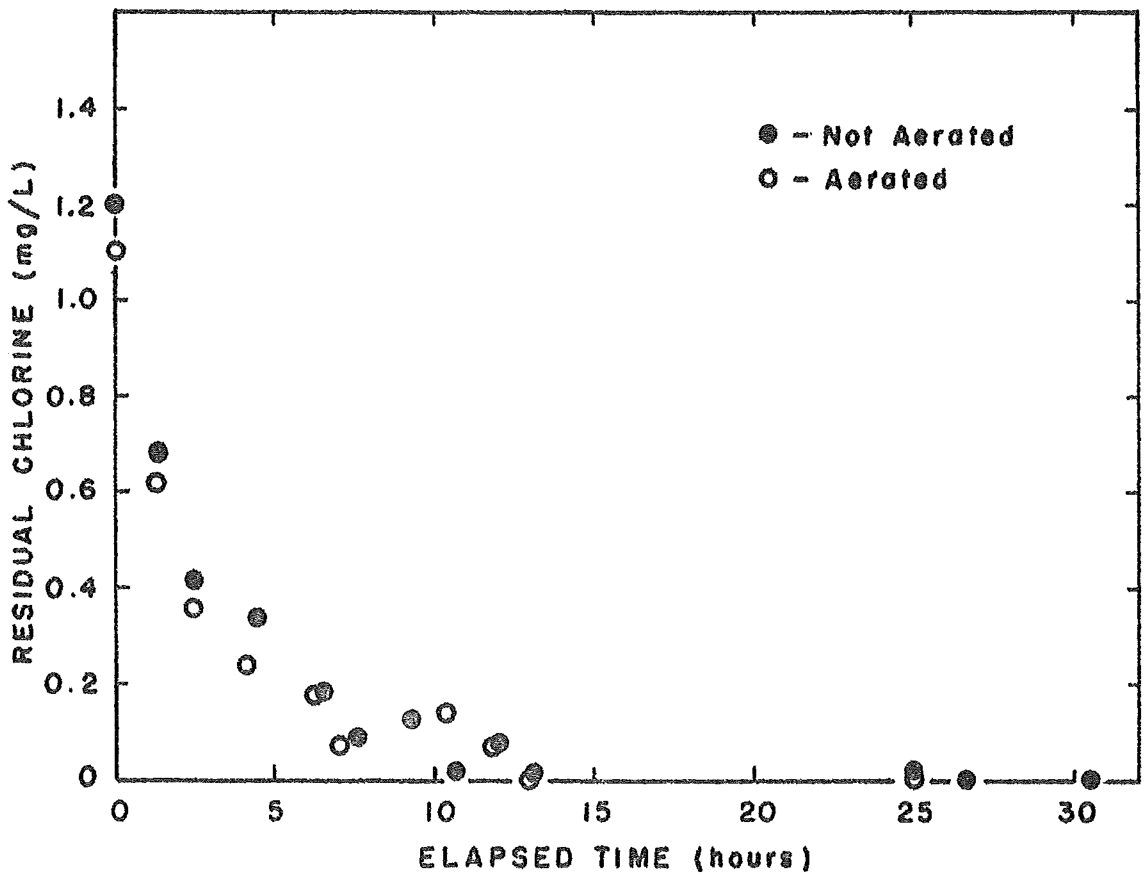

FIGURE 1 - Decay of chlorine residuals in sewage.

DISCUSSION

Toxicity of Primary, Chlorinated and Dechlorinated Sewage

The 96 hour LC50 of primary sewage to sockeye salmon at Lulu Island was previously reported between 10 and 25% v/v (Martens and Servizi, 1974) and similar results were found during six of seven bioassays reported herein. Sockeye fingerlings appeared more sensitive to acute toxicity of sewage than pink salmon fry. This was confirmed by statistical comparison of MST's of sockeye and pink salmon using Student's "t" test ($p = 0.01$ to 0.05). Similar results were reported for in-stream bioassays of chlorinated municipal sewage where sockeye fingerlings were more sensitive than pink salmon alevins (Servizi and Martens, 1974). However, it should be noted that pink salmon alevins were more sensitive than sockeye alevins when exposed to chlorinated catechols (Servizi, Gordon and Martens, 1968) and neutralized kraft bleach plant wastes (Servizi, Stone and Gordon, 1966).

Methylene Blue Active Substance (MBAS) and ammonia were cited as causing about 67% of acute toxicity of primary sewage in the San Francisco area, while heavy metals and reduced substances were believed to account for 33% of acute toxicity (Esvelt, Kaufman and Selleck, 1973). Anionic surfactants averaged 4.47 mg/l and ranged from 2.2 to 8.8 mg/l in primary sewage at Lulu Island. The average value was about half the value of MBAS measured in San Francisco area primary sewage. However, surfactants probably contributed to acute toxicity of sewage at Lulu Island, since the acutely toxic concentration reported for surfactants is 2 to 6 mg/l (Esvelt, Kaufman and Selleck, 1971).

Ammonia nitrogen concentration (mean 18.5 mg/l) and acute toxicity of sewage in the San Francisco area were strongly correlated (Esvelt, Kaufman and Selleck, 1973). Ammonia nitrogen concentrations were slightly greater at Lulu Island, thus it is assumed that ammonia contributed to toxicity of primary sewage at Lulu Island. However, the toxicity of ammonia has been reported as related to the un-ionized ammonia concentration (McKee and Wolf, 1963), which is in turn dependent upon pH and temperature. Calculation of un-ionized ammonia according to Trussel (1972) indicated that concentrations in both Lulu Island (TABLE 2) and

San Francisco primary sewages (Martens and Servizi, 1974) were less than levels of un-ionized ammonia assumed lethal (0.2 to 0.9 mg/l NH_3) by Esvelt, Kaufman and Selleck (1971). In view of the strong correlation reported between ammonia nitrogen and toxicity, factors in addition to un-ionized ammonia may be associated with toxicity of ammonia and warrant further study.

Since the metals content of primary sewage reported herein was similar to that reported for the previous study at Lulu Island, contributions toward total toxicity of sewage were probably similar. Both total extractable and dissolved metals were measured in the latest study since for some metals the latter is considered the principal toxic form. For example, ionic copper (Cu^{++}) is considered biologically more active than copper carbonate ($CuCO_3$) (Lloyd, 1965). Dissolved copper was frequently present in excess of the lethal level and cadmium was sometimes in excess of the lethal level (Servizi and Martens, 1971). Based upon information available, there is a possibility that iron levels were high enough to be toxic to salmon, but the remaining metals measured were present at concentrations less than those reported acutely toxic (McKee and Wolf, 1963).

Cyanide is reported lethal to rainbow trout and brook trout (Salvelinus frontinalis) at concentrations as low as 0.05 mg/l in five to six days (McKee and Wolf, 1963). Cyanide concentration in Lulu Island sewage averaged 0.11 mg/l and ranged from less than 0.03 to 0.36 mg/l. The average cyanide concentration was thus likely to have been lethal to test fish.

Nitrite concentrations averaged 0.04 mg/l and ranged from less than 0.005 to 0.08 mg/l in Lulu Island sewage. An LC50 concentration of 0.23 mg/l nitrite for rainbow trout (Salmo gairdneri) was reported by Brown and McLeay (1974). Smith and Williams (1974) report 55% mortality of rainbow trout at 0.55 mg/l nitrite following a 24 hour exposure and 40% mortality of chinook salmon (O. Tshawytscha) at 0.50 mg/l nitrite following a 24 hour exposure. Thus nitrite concentrations in Lulu Island sewage were probably less than acutely toxic.

However, both of the aforementioned reports indicate a substantial decrease in blood hemoglobin and formation of methemoglobin at sublethal nitrite concentrations. Brown and McLeay (1974) report a 20% reduction in blood hemoglobin at 0.05 to 0.10 mg/l nitrite. Since nitrite concentrations in sewage at Lulu Island were within this range, an increase in methemoglobin may have occurred in test fish during bioassays. Increased blood methemoglobin may reduce tolerance of fish to toxicants which act by causing damage to the gill epithelium and subsequent impairment of gas exchange at the gill epithelium.

A large increase in toxicity of treated sewage following disinfection with chlorine has been documented (Esvelt, Kaufman and Selleck, 1971; Tsai, 1971; Zillich, 1972; and Martens and Servizi, 1974) and a similar increase in toxicity was observed in this study. However, chlorine induced toxicity was removed by application of sulfur dioxide. Furthermore, dechlorinated primary sewage was less toxic than primary sewage, suggesting degradation of some toxic constituents by the chlorination-dechlorination process. The reduction in toxicity was of limited practical significance since the lowest concentration at which mortalities occurred was 17% v/v for both primary and dechlorinated sewage. Esvelt, Kaufman and Selleck (1973) also reported a net reduction in acute toxicity following dechlorination with sodium bisulfite.

Chlorinated Organics

It is recognized from experience with pesticides that many chlorinated organic compounds have a profound effect upon aquatic life. It is now evident that approximately 1% of chlorine applied during treatment of municipal sewage occurs as stable chlorine-containing organic constituents (Jolley, 1975). Studies showed that two such compounds, 5-chlorouracil and 4-chlororesorcinol, significantly decreased hatchability of carp (cyprinus carpio) eggs at concentrations as low as 0.001 mg/l (Gehrs et al, 1974). Thus, although dechlorination is useful and necessary in reducing hazard of chlorinated sewage to aquatic life, it cannot be considered a panacea. Furthermore, the potential effects on aquatic life of chronic low-level dosages of chlorinated organic constituents cannot be overlooked and deserve further study.

Toxicity of Sulfur Dioxide

When sewage is dechlorinated using sulfur dioxide, residual sulfur dioxide can be expected. At neutral pH, sulfur dioxide exists primarily as sulfite ion which oxidizes to sulfate ion, extracting dissolved oxygen from an aqueous solution in the process. Trout were reported killed by 5 mg/l sulfur dioxide in one hour but conditions of pH and dissolved oxygen were not reported (McKee and Wolf, 1963). On the other hand, Dean (1974) advised, when commenting on dechlorination, that there are no toxic effects from slight excesses of sulfur dioxide. In the studies reported herein, fish were exposed to an average of 0.81 mg/l sulfur dioxide residual with a range from 0.09 to 2.30 mg/l without noticeable effect. In order to test for possible toxicity caused by sulfur dioxide, the system was adjusted to maximum delivery, giving a mean residual of 2.20 mg/l SO_2 for 96 hours. There was no indication that over-sulfonation to this degree increased acute toxicity of dechlorinated sewage over that of primary sewage.

Dissolved Oxygen and pH

There was no noticeable effect on pH or dissolved oxygen caused by dechlorination using sulfur dioxide (TABLE 5). However, sulfuric and hydrochloric acids are formed during reaction of sulfur dioxide with chlorine and dissolved oxygen in sewage and stoichiometric calculations using equations (1) and (4) can be used to estimate the alkalinity consumed. Assuming dechlorination of 2 mg/l chlorine residual with an excess of 1 mg/l SO_2, about 7.3 mg/l of alkalinity ($CaCO_3$) are consumed. This is a small amount compared to an average alkalinity of 117 mg/l (TABLE 2). Oxygen consumed by 1 mg/l excess sulfur dioxide was estimated as 0.25 mg/l using equation (4) and would not be readily detected since reaeration in the contact channel would tend to replace dissolved oxygen consumed. In view of the foregoing it appears that pH adjustment and reaeration may not be needed in every case. However, in the event that aeration may be required, combining the functions of sulfur dioxide dispersion and aeration using a turbomixer may be a practical solution.

Cost of Dechlorination

The cost of disinfection with chlorine at Lulu Island was 0.89¢/1,000 U.S. gal, using data supplied by GVSDD. Chlorine cost was $140 per ton. The cost of dechlorination estimated by GVSDD was 0.97¢/1,000 U.S. gal, including labor, power, amortization of capital and sulfur dioxide in one ton cylinders at $189 per ton. The GVSDD estimate cost of sulfur dioxide at Lulu Island treatment plant will decrease to about $96 per ton when facilities are completed at the new Annacis Island treatment plant to handle sulfur dioxide in bulk for resupplying Lulu Island. The bulk price of SO_2 is about $71 per ton. When the Lulu Island plant reaches design flow of 16 U.S. MGD the cost of dechlorination is estimated at 0.322¢/1,000 U.S. gal. Dechlorination at the Annacis Island plant was projected at 0.282¢/1,000 U.S. gal.

Dean (1974) estimated that disinfection followed by dechlorination using sulfur dioxide should cost not more than 1.3 times the cost of disinfection and may be as low as 1.2 times that cost. However, local costs of chemicals can be expected to affect these ratios.

Costs were itemized in a comprehensive study of chlorination, dechlorination and post aeration to 4 mg/l D.O. (Smith, Eilers and McMichael, 1974). Post aeration was costly and estimated at 1.57 to 3.94 times the cost of dechlorination using sulfur dioxide. Judging from experience at Lulu Island treatment plant, post aeration would not be required in every case, thereby avoiding significant added cost.

Alternative Methods of Dechlorination

In addition to sulfur dioxide, sodium metabisulfite and sodium sulfite are dechlorinating agents and may prove suitable at small installations. However, dechlorination may also be accomplished by activated carbon or lagooning. Free chlorine and chloramines react with activated carbon and the potential exists for removing ammonia as well as chlorine in the process (Snoeyink and Markus, 1974). However, costs of dechlorination using activated carbon were 13 to 20 times the cost of dechlorination using sulfur dioxide (Smith, Eilers and McMichael, 1974).

Chlorine residuals disappeared during lagooning and effluents were not acutely toxic to salmon after 30 to 60 days detention (Servizi and Martens, 1974). Comparison of water quality and fish populations in the vicinity of secondary sewage treatment plants showed that dechlorination of effluents in lagoons before discharge safeguarded the general fish population (Tsai, 1971). Data reported herein indicated chlorine residual disappeared within 13 hours for a sample of chlorinated sewage with a chlorine residual about 55 to 60% of the mean. On the other hand, more than three days were required for chlorine residuals to decay to low levels in samples from other treatment plants (Servizi and Martens, 1974; Esvelt, Kaufman and Selleck, 1973). It is evident that further work is required to define the optimum detention time required for dechlorination in lagoons. However, lagooning should not be overlooked as a method of dechlorination since it appears dependable and economical for small plants where land requirements are not large.

CONCLUSIONS

1. Primary treated sewage at Lulu Island was acutely toxic to sockeye and pink salmon at concentrations as low as 17% v/v sewage. The 96 hour LC50 was most frequently between 17% v/v and 25% v/v sewage.
2. Disinfection by chlorination greatly increased acute toxicity of sewage to sockeye and pink salmon.
3. Dechlorination using sulfur dioxide removed chlorine induced acute toxicity but dechlorinated primary sewage remained acutely toxic to sockeye and pink salmon.
4. Sulfur dioxide residuals averaging 2.20 mg/l did not increase the acute toxicity of primary sewage to sockeye or pink salmon.
5. Dissolved oxygen and pH were not adversely affected by dechlorination using sulfur dioxide at Lulu Island treatment plant.

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