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Summary Report of Research Conducted on the Lower Fox River by Staff of the Environmental Research Laboratory-Duluth, and by Personnel on Cooperative Agreements.

DATE ?. 1986

by

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Introduction

The Lower Fox River, located in northeastern Wisconsin, is a major tributary to Green Bay in Lake Michigan. It is ~ 64 km long from Lake Winnebago to Green Bay, drains an area of 40,000 km^2, and is one of the most heavily industrialized rivers in the country. There are 15 pulp and/or paper mills, 8 municipal waste water treatment plants and one electrical generating station (Toxic Substances Task Force, 1983) on the river. The Fox River has had a long history of organic pollution dating from soon after the turn of the century when the pulp and paper industry started; this resulted in the construction of dams for power, locks, and navigational channels. The disposal of industrial and municipal wastes resulted in increased biological demand (BOD) and fish die-offs as early as 1924 (Patterson 1980). Conditions began to improve as industries installed secondary treatment in the early 1970's, prompted in part by the Federal Water Pollution Control Act Amendment of 1972. A continued effort by industries and various local and government control agencies has resulted in great improvement in water quality. However, problems remain particularly with xenobiotic compounds of which 105 organic compounds have been identified from biota, water, sediment and effluent discharges (Wisconsin Department of Natural Resources 1978). Many of these organic compounds are known or suspected carcinogens and are of direct concern to man; however, their effect on the aquatic biota is largely unknown.

Results

An annotated bibliography of 75 papers compiled by Lozano (1985) was used to identify potentially hazardous toxicants on the Lower Fox River (see Appendix A). This was intended to be used to apply existing fate and transport models as well as to develop new models to assist regulatory decision makers in planning mitigation strategies. However, studies concurrently being conducted did not show general patterns of toxicity and so the modeling was not developed.

Lozano (1985) summarized some of the literature and stated that dissolved oxygen levels responded well to clean-up measures although summer oxygen levels in some sections of the river drop below 2 mg/l and occasionally to < 1 mg/l. The benthic fauna has not yet recovered in many sections of the river and is characterized by fauna which tolerate high organic sediment levels and low dissolved oxygen.

Chemical compounds which might have an effect, as reported by Sullivan and Delfino (1982), include: chloroform, trichloroethane, abietic acid, isopimaric acid, linoleic acid, linolenic acid, Bis (2-ethylhexyl-phthalate), and arsenic, cadmium, chromium, copper, cyanide, lead, nickel, mercury and zinc. Effluent concentrations of PCBs in effluents of 0.1-56 $\mu g/l$ were reported; the average water concentration in 1982 was 0.097, although levels of 0.85 $\mu g/l$ were detected near pulp and paper mills. Sediment levels are usually between 0.05-61 $\mu g/l$ dry weight as reported from the literature by Lozano (1985).

Effluent, Instream and Sediment Toxicity

To test for possible toxicity of efluents, water quality instream and sediments, a series of bioassays was made in 1983 and again in

1985. Industrial and municipal effluents discharging into the Lower Fox River were tested in 1983 (Anon, 1983) for toxicity using seven day ceriodaphnid (Ceriodaphnia dubia), and seven day fathead minnow (Pimephales promelas) tests. Effluent samples were collected continuously over a twenty-four hour period, whereas dilution water was collected each day as a grab sample immediately upstream of the discharge. Solutions for both species were changed daily. A map showing the location of the discharges is given in Appendix B-1 and a summary of the test results is given in Appendix B-2. Toxic dilution water from just above the effluents was frequently found. In 12 of the 18 effluent tests the dilution water was either toxic, or suspected of being toxic, to one of the test organisms. However, both species did not show marked toxicity on the same sample. Many of the effluents mitigated the toxicity of the ambient water. In general, effluents which were successfully tested showed low toxicity; ambient toxicity could not be attributed to any one effluent.

The water from ten instream (ambient) stations (see Appendix B-1) was tested with ceriodaphnids and fathead minnows in March and April 1983 (Anon 1983). There were no adverse effects except at one station on 4/29/83. Some stimulation of growth and reproduction occurred at all stations on 3/24/83. Water and sediment grab samples were collected from the Lower Fox River in January, March and April, 1985 from instream areas not located near effluents (see Appendix B-3). Laboratory bioassays were conducted on river water, elutriate water from the sediment, and in water with sediment added to evaluate their potential toxicity (Lien et al. 1986). Daphnid (Daphnia magna) acute tests, fathead minnow seven day survival and growth tests, and ceriodaphnid survival and reproduction tests were conducted on river water from the various stations. There were no significant adverse effects on survival of these organisms during the test periods. However, growth of fathead minnows was significantly less at Station D collected in January. Water collected in March significantly reduced ceriodaphnid reproduction at most stations when compared to reference stations although the reduction was not considered biologically important (e.g., a reduction of young from about 28 to about 22 in seven days). The general water chemistry results for those tests are given in Appendix B-4.

Acute (2-day) and chronic (10-day) daphnid bioassays were run on elutriate water. Daphnids in two of three replicates at station K in April died in the chronic test, but since the third replicate had 100% survival and good young production, something other than a toxicant effect was suspected. Waters from Station G in March and K in April produced significantly fewer young than the reference station.

Ten day daphnid and Hyalella bioassays were conducted in Fox River water over sediments (solid phase test) from the same stations. Survival and reproduction of daphnids was often less for the reference stations than for the other stations. Water in the solid phase test was not toxic to daphnids nor to Hyalella azteca. Sediment samples were collected as grab samples using an Ekman dredge. The hard rocky bottoms at Stations H and M prevented sampling at these locations. The depth of the river where samples were obtained varied from 0.9 to 7.6 m (see Lien et al. 1986).

Concentrations of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and tetrachlorobiphenyls in these sediments are given in Table 1. Locations of the sampling stations are given in Appendix B-3. Stations D and J tended to have the highest concentration of tetrachlorobiphenyls. The methods of measuring these compounds and the quality control are given in a report by Gross (1986).

Walleye Ova and Larval Survival and Growth

Contaminant effects on walleye reproduction were investigated by collecting walleye from two areas known to have high concentrations of organic pollutants and one area considered to be relatively clean. Walleye brood stocks were collected from below the DePere Dam on the Fox River and Sturgeon Bay on Green Bay, Wisconsin; a control stock was collected from the Chippewa Flowage in Wisconsin. Walleye eggs were stripped and fertilized and shipped to the Environmental Research Laboratory-Duluth for incubation in Lake Superior water (Hokanson and Lien, 1986). Ova fertility was determined and the number of normal, deformed and dead yolk-sac larvae were counted at the time of hatch. Larval walleye were fed and reared under optimum conditions for three weeks; measurements included survival, total length and dry weights at specific time intervals (first feeding, resorption of the oil globule, commencement of the juvenile phase), and at the termination of the study.

Larval survival at the post-larval I phase of development (Appendix B-5) was significantly higher from the Chippewa Flowage stock (90.8%), than from the Fox River (73.3%) and Sturgeon Bay (58.9%) stocks. Walleye survival was highest in the pro-larval and juvenile phases of development and lowest for the post-larval I phase. The latter period of development is one of the most critical stages when contaminant-induced mortality is expected to be the highest. Additional evidence of a contaminant problem was evident from the relationship between biological effects and the size of the females. Post-larval I developmental phase survival was negatively correlated with adult female weight.

Overall larval survival was lowest from the Sturgeon Bay stock and highest in the control stock from the Chippewa Flowage, although there was no significant difference.

Embryo survival to hatch varied from 32.9% for the Lower Fox River to 72.6% for Sturgeon Bay to 85.7% for the Chippewa Flowage stock. The Lower Fox River stock had significantly lower embryo survival than the other two stocks which reportedly was due primarily to differences in the fertility of the ova. Fertility of ova was 46.5%, 79.1% and 88.6% for stocks from the Lower Fox River, Sturgeon Bay and Chippewa Flowage respectively.

The walleye adults and ova used for the study in 1985 were analyzed for dioxins, furans and biphenyls. Concentrations in whole fish and ova are given in Table 2. (See report by Gross, 1986, for analytical methods and quality control.) Concentrations of dioxins were generally higher from Sturgeon Bay walleye, whereas, concentrations of furans were higher from Fox River walleye. Hokanson and Lien (1986) are currently analyzing the data and looking for correlations between chemical body burdens and biological effects. Also given in Table 2 are concentrations of certain pesticides and PCBs found in fish collected in 1983 from the Lower Fox River (see report by Duke, 1984).

Auer and Auer (1986) studied the impact of river water quality on walleye egg development not influenced by fungal infestation, predation or siltation. They collected and fertilized eggs from the

Fox River and placed them in river water in dialysis tubes which were rotated in a large tank receiving a continuous flow of Fox River water. Incubation was conducted in a mobile laboratory at the edge of the Fox River on the grounds of the DePere, Wisconsin, waste water treatment plant. Egg survival to hatch on day 7 ranged from 34 to 82% with a mean of 60%. All hatched larvae attained lengths of 8.5 to 10 mm after 5 days, although feeding was not observed. Chemical conditions of the river water during egg incubation period are given in Appendix B-6.

Water samples throughout the water column were collected on 21 April and 9 May, 1983 to characterize spatial heterogeneity (Auer and Auer 1983). Samples were collected at 5-10 cm intervals beginning at 5 cm above the bottom. Chemical measurements showed little variation with depth in dissolved oxygen, pH or dissolved sulfides. Dissolved oxygen was near saturation, pH was from 8.1-9.2 and hydrogen sulfide was < 0.001 $\mu g/L$.

Sediment water chemistry at the sediment water interface during the summer months of 1985 revealed dissolved oxygen ranging from 0.16 mg O_2/L at sites with highly organic sediments to 7.2 mg O_2/L with sandy sediments; pH ranged from 7.22-8.45 (Auer and Auer 1986). Ammonia and nitrite nitrogen, and hydrogen sulfide ranged from 0.073-2.372 mg N/L, 0.015-0.067 mg N/L and 0.0018-0.2899 mg/L, respectively. Sediment chemical oxygen demand (COD) near DePere ranged from 6-463 mg O_2/g DW (see Appendix B-7).

Regions of the Lower Fox River sediment COD are classified in Appendix B-8, B-9 and B-10, over ranges of 0-50, 51-100, 101-170 and > 170 mg $O_2/9$ DW (Auer and Auer, 1983). In general, only suitable walleye spawning and egg development was observed over sediments having a chemical oxygen demand less than 50 mg O_2/g DW where dissolved oxygen, ammonia, nitrogen, and hydrogen sulfide concentrations were suitable. Balcer et al. (1986) reported that areas with less than 50 mg O_2/g DW have sand and gravel substrates and are suitable for walleye ova incubation, whereas levels greater than 100 mg O_2/g DW are correlated with organic muck and soft clay which is not suitable for incubation of walleye eggs.

Balcer et al. (1986) collected adult walleye from the Fox River, stripped and fertilized their eggs. They incubated the eggs in-situ in the Fox River using incubation trays, tissue culture plates, incubation tubes, dialysis bags and on artificial reefs. Walleye ova survival for eight days (until just before hatching) was 20%, 35% and 25%, respectively, for the incubation trays, tissue culture plates and incubation tubes. These investigators found no significant difference between ova incubated in mid-water and those incubated on the bottom in areas of low COD; this indicated that at suitable spawning sites physical and chemical conditions were adequate for walleye ova incubation throughout the water column.

In 1986, ova were collected from walleye from the Lower Fox River (Brooke, 1986); the fertilized ova were placed in tissue culture plates and ova incubation trays and incubated on the river bottom at ten sites located between the DePere Dam and the Fort Howard Paper Company to evaluate the impact of substrate quality and ova survival (Appendix B-11). A subset of the incubators was lifted periodically for grooming and examination of ova development. The 10 incubation sites differed with respect to current velocity and substrate type, ranging from areas with rapid currents and cobble substrates (sites 8 and 9) to backwater areas with reduced flow and fine organic substrates (sites 7, 10 and 12). All sites had similar values for pH (8.1-8.8), conductivity (230-330 umho/cm^2), total alkalinity (140-160 mg/L $CaCO_3$) and EDTA hardness (160-195 mg/L $CaCO_3$). Oxygen remained near saturation at the bottom at all sites throughout the incubation period. Although nitrite and sulfide were only at the detection limit, high ammonia concentrations ($\geq$ 0.3 ppm) were consistently found at site 4, below the DePere Treatment Plant. Ova survival at the incubation sites was variable. Although no statistical analyses have been made, examination of the survival data from non-groomed tissue culture plate incubators (Appendix B-12) suggested that survival of walleye ova in the Lower Fox River was maximal near the DePere Dam (sites 8, 9 and 11) and below the Hwy 172 bridge (site 2). Ova survival was reduced at sites 4, 5 and 6 (between the Brown County Fairground and the DePere Treatment Plant) and was extremely poor at sites with fine organic substrates (sites 7 and 10). Data from ova pumping, drift netting and ova collection hoops indicated that walleye in the Lower Fox River used the cobble areas below the DePere Dam (sites 8 and 9) as primary spawning grounds and that survival of naturally spawned ova is good at oviposition sites.

Balcer et al. (1986) collected eighteen species of fish in the Lower Fox River in April of 1985 (Appendix B-13). Walleye and yellow perch were the most abundant species and spawned in the river. Thirty-eight of the 643 adult walleye examined had lymphocystis-like growths and tumors. The growths were more common to males than to females and were most prevalent on the fins and opercula.

Work Underway or Planned

Walleye adults and ova from the Fox River have been analyzed for dieldrin; p,p DDE; p,p DDD; p,p DDT; cis-chlordane; cis-nanochlor; trans-nanochlor; Araclor 1248; and Araclor 1254. Analyses of polychlorinated dibenzo-p-dioxins (PCDDs); polychlorinated dibenzofurans (PCDFs); and tetrachlorobiphenyls (TCBs) in walleye, walleye ova and sediment have recently been completed. Preliminary results are included in this report. An investigation is currently underway to determine whether or not observed biological effects can be correlated with chemical residues.

Work proposed, but not completed, includes the following: (1) use of in-situ biomonitoring tools to identify problems limiting survival and the distribution of sensitive benthic macro-invertebrates; (2) in-situ synoptic surveys of benthic macroinverte-brates along a pollutant gradient to identify species and classify each into functional ecological guilds reflecting environmental requirements; (3) investigation of a possible correlation between organic contaminant levels in ova and adult walleye and biological effects on larval walleye; and (4) measure organic contaminants in edible fish which threaten human health.

Studies should include development of a toxic residue model to ascertain the origin of and to predict the fate and effects of toxicants which bioaccumulate in the food chain from the Fox River and Green Bay. The focus should be on the bioconcentration/ bioaccumulation of toxicants suspected or known to adversely affect or threaten birds and humans consuming fish.

Studies could also possibly include modeling the biological (BOD) and chemical (COD) oxygen demand of the sediment, including the origin of the materials contributing to the demand as well as the time required to achieve suitable spawning substrate if certain sources were reduced or eliminated.

Summary and Conclusions

Effluents entering the Lower Fox River, which were tested in 1983, were often non-toxic to fathead minnows and ceriodaphids although many tests were not successful because of the toxicity of the water upstream from the effluents. It was concluded that, with some reservations, some effluent additions may reduce ambient toxicity. Laboratory studies on instream (ambient) Fox River water using fathead minnows, daphnids, and ceriodaphnids in 1985 did not show lethal effects although there were some subtle chronic effects on fathead minnow growth and ceriodaphnid reproduction. Results of these tests indicated sources of toxicity periodically but not consistently. In evaluating these laboratory tests the inherent limitations of the test results should be considered. Temporary changes in the water quality are not apparent from grab samples taken at a particular time. In addition, prolonged storage of samples, aeration (which would remove volatile compounds) and changes in temperature all change the physical and chemical characteristics of the water. It is apparent that *in situ* bioassays and instream identification and enumeration of the biota would more accurately evaluate the present condition of the Fox River, which has not yet recovered from years of degradation. The benthic fauna inhabiting the soft substrates of the lower Fox River were comprised mainly of chironomids and oligochaetes (Markert, 1981), although some caddisflies had become more common by 1980. It is evident that a survey of the bottom fauna is again needed.

Instream water quality measurements for pH, alkalinity, conductivity, hardness, chloride, nitrite and nitrate nitrogen, phosphorus, sulfate, sulfides, and ammonia have shown that these parameters were suitable for aquatic life. However, in the lower Fox

River sediment concentrations of ammonia-nitrogen, hydrogen sulfide and dissolved oxygen were not suitable for fish egg development. Areas with high sediment chemical oxygen demands had sulfide concentrations of ~ 0.3 mg/L, ammonia-nitrogen concentrations from 2-5 mgN/L and oxygen concentrations of < 3 mg/L (Auer and Auer, 1986). Acute and chronic toxicity standards were exceeded in over 50% of the samples analyzed. These areas were chemically unsuitable for fish egg development and for many macroinvertebrates. In addition these sediments contained many chemicals which bioaccumulate in aquatic animals. Additional analysis of toxic materials in the sediment, as well as a scheme to deal with this problem, is needed.

Recent studies summarized in this report showed that eggs from walleye were viable when incubated in Lake Superior water, Fox River water, on artificial substrates on Fox River sediment, and naturally on Fox River sediment with a COD of < 50 mg O_2/g DW. Approximately 35% of the sediment of the lower Fox River has COD concentrations suitable for walleye spawning. In 1985 the walleye successfully reproduced naturally in the lower Fox River. However, there was evidence that contaminants were affecting reproduction. The negative relationship between larval survival and female weight suggested a contaminant problem as larger fish were known to have larger amounts of toxicants which bioaccumulate. The biological effects were evident in fish from the lower Fox River and also from Sturgeon Bay in Lake Michigan. Mortality of walleye was highest in postlarval 1 phase of development when the yolk sac was absorbed. As the yolk sac is the primary storage site for chlorinated hydrocarbons this is the time when these compounds would be transferred to the larval fish. In addition to contaminants present in fish, unsuitable temperatures because of unsuitable weather and fluctuations from seiche activity may also contribute to year-class failures of walleye. In 1985 and 1986 there was successful walleye reproduction in the Lower Fox River as water temperatures rose and other conditions were suitable. Toxicants alone therefore are not responsible for walleye reproductive failures, but further decrease environmental resistance. Restoration of suitable sediment and lowering of organic contaminants in the fish brood stock would provide for a better hatch, especially in years when incubation conditions are marginal.

Additional research needed on the Fox River includes more extensive sediment analysis for other chemicals, in situ biomonitoring and surveys, investigating a possible correlation between concentrations of organic contaminants in Fox River and Green Bay fish and effects on larval fish survival, development of a toxic residue model focusing on bioaccumulation of toxics known or suspected of causing adverse effects to aquatic life, birds and man and a model for the biological and chemical oxygen demand to predict adverse effects and to predict the consequences of removing or eliminating certain sources.

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Wisconsin Department of Natural Resources. 1978. Investigation of chlorinated and nonchlorinated compounds in the Lower Fox River watershed. EPA-905/3-78-004. U.S. Environmental Protection Agency, Chicago, IL. 229 pp.

Table 1 Concentrations of Polychlorinated Dibenzo-p-dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and Tetrachlorobiphenyls (TCBs) in Sediment Samples from the Lower Fox River Collected in January, March and April, 1985[a]

Sampling Stations	A	B	C	D	E	F	G	H	I	J	K	L	M
TCDD ppt	ND	10	ND	35	3	ND	8 5	-	ND	40	ND	ND	-
P5CDD ppt	27	45	45	35	110 0	4 0	ND	-	ND	700	ND	ND	-
P6CDD ppb	6.6	1.0	5 5	1 8	0 07	0 25	0 7	-	-	6 6	0 07	0.2	-
P7CDD ppb	6	11 5	8 0	13 7	4 0	3 2	9 0	-	14	96	0 7	0.45	-
OCDD ppb	8 7	9 0	20 0	45 3	3 2	6 0	23 5	-	43	315	1 5	1.4	-
TCDF ppt	47 5	25	37 5	90 0	6 0	8 0	27 5	-	50	45	4	15	-
P5CDF ppt	15	15	20	55	ND	ND	ND	-	ND	ND	ND	ND	-
P6CDF ppb	0 3	0 6	0 4	0 7	0 04	0 09	0 6	-	-	1 2	0 02	0 07	-
P7CDF ppb	4 6	4 2	3 3	4 3	1 4	0 7	5 0	-	3 2	44 0	0 1	0.2	-
OCDF ppb	0 6	0.3	0 8	2 7	0 25	0 2	0 4	-	1 0	25 0	0 03	0 07	-
3,4,3'4'-TCB ppb	7 6	6 2	7 1	61 0	ND	0 41	13 0	-	0 25	0 21	0 54	0 01	-
Total TCB ppb	120	11	208	3,400	14	0 52	5 60	-	0 39	0 13	0 7	0 13	-

[a] Concentrations for Stations A and D are the mean of three samples taken in January, March and April, concentrations for Stations B and C are the mean of two samples taken in January and March, whereas, concentrations for other stations are from samples taken in April in 1985 For station locations see Appendix B-3

Table 2 Concentrations of Dioxins, Furans, Biphenyls and Pesticides in Adult Walleye and Walleye Ova[a]

Chemical	Fox River Fish: No above detection limits	Fox River Fish: X amount in tissue Range	Fox River Fish: Ova[a] X	Sturgeon Bay Fish: No above detection limits	Sturgeon Bay Fish: X Range	Sturgeon Bay Fish: Ova[b] X	Chippewa Flowage Fish: No above detection limits	Chippewa Flowage Fish: X Range	Chippewa Flowage Fish: Ova[b] X
TCDD ppt	All	3.5 (2.5-4)	1 9	All	3 2 (3-4)	1 8	None	-	ND
P5CDD ppt	None	-	ND	None	-	ND	None	-	ND
P6CDD ppt	5	6 9 (4-10)	ND	3	23 7 (9 50)	20	None	-	ND
P7CDD ppt	All	37.1 (2-70)	31 1	All	44 7 (15-45)	13 0	All	15 3 (5-45)	19 5
OCDD ppt	All	55 3 (15-130)	66 9	All	65 (40-105)	45 0	All	53 3 (30-90)	60
TCDF ppt	All	37 1 (30-40)	18 5	All	36 (30-40)	16 8	None	-	ND
P5CDF ppt	All	11 3 (3-25)	1 4	All	11 7 (8-22)	4 3	None	-	ND
P6CDF ppt	5	12 6 (4-25)	19 5	All	7 5 (3-6)	2 5	None	-	ND
P7CDF ppt	6	15 7 (10-25)	11 8	All	9 8 (7-18)	4.7	All	12 2 (4-45)	7
OCDF ppt	5	7 4 (1-25)	4 9	All	13 2 (5-30)	6.3	All	11 5 (4-20)	5
3,4,3'4'-TCB ppb	3	35 7 (22-45)	50	All	39 2 (30-60)	27 3	All	0 42 (0 02-1 0)	05
Total TCB ppb	All	4,912 6 (77-16,000)	1131 2	All	1486 7 (940-2200)	1390	All	8 5 (2-23)	3 5
o,p DDE ppm	1	0 6	ND						
p,p DDE ppm	All	0 76 (0.48-1 5)	0 43						
o,p DDD ppm	None	-	ND						
p,p DDE ppm	6	0 10 (0 07-0 15)	0 06						
o,p DDT ppm	None	-	ND						
p,p DDT ppm	1	0 14	ND						
c chlordane ppm	5	0 06 (0 05-0 14)	0 06						

+ chlordane ppm	None	-	ND
c nanochlor ppm	3	0 07 (0 05-0 10)	ND
+ nanochlor ppm	6	0 12 (0 07-0 22)	0 08
PCB 1248 & 1254 ppm	All	14 9 (10-21)	13 9
Dieldrin ppm	All	1 23 (0 03-8 3)	0 04

[a] Measurements were made on seven fish from the Fox River, six fish from Sturgeon Bay and six fish from the Chippewa Flowage

[b] Mean values only - numbers above detection and range not included

APPENDIX A

ANNOTATED BIBLIOGRAPHY

AHNOFF, M., B. JOSEFSSON, G. LUNDE, and G. ANDERSSON

1979

MONITORING OF TOTAL AMOUNT OF LIPOPHILIC ORGANO CHLORINE COMPOUNDS IN A SWEDISH RIVER

WATER RES. 13:1233-1237

A sensitive method for the determination of organic bound chlorine in river water has been used in a monitoring program. The amount of organic bound chlorine, extracted by cyclohexane and determined by neutron activation analysis, was chosen as a parameter for detection and tracing of pollutants with annoying or harmful properties. During one year, 216 samples, each collected continuously during 48 h. were taken at seven stations, located at 7-23 km distance along the Gota River, Sweden. The detection limit of the method was below 0.05 ug $Cl l^{-1}$. Major sources of pollution were localized to certain sections of the river.

W.F. AHRNSBRAK AND R.A. RAGOTZKIE

1970

MIXING PROCESSES IN GREEN BAY

PROC. 13TH CONF. GREAT LAKES RES. 880-890. INTERNAT. ASSOC. GREAT LAKES RES.

A one-dimensional diffusion model based on the principle of conservation of mass is applied to Green Bay. Observed diffusivities are compared with those predicted on the basis of seiche activity and that mechanism is shown to be primarily responsible for the observed concentration field. Diffusivities in the vicinity of Long Tail Point are on the order of 0.25×10^6 cm^2/sec with an abrupt jump to 1×10^6 cm^2/sec a few km beyond and gradually increasing to 2 to 3×10^6 cm^2/sec in the central part of the Bay. Electrical conductivity and light transmissivity are used to observe the distribution of Fox River water in the Bay. Highest concentration gradients (40% km) were found in the vicinity of Long Tail Point and along the eastern shore of the southern end of the Bay. No appreciable transferse gradients were found in the mid and northern portion of the Bay. (Key words: Diffusion; pollution; seiche; Green Bay.)

ANDERSON, R.V.

1977

CONCENTRATION OF CADMIUM, COPPER, LEAD, AND ZINC IN SIX SPECIES OF FRESHWATER CLAMS

BULL. ENVIRON. CONTAM. TOXICOL. 18(4):492-496

In summary the metal concentrations in the bodies of the freshwater clams studied generally reflected that found in the environment, with the exception of Zn. The shell had comparatively lower concentrations of all metals which reflects its inactive role in filtering and feeding. While concentrations of the studied metals are not the same between saltwater and freshwater clams the relationships between the metals, body parts, and environment were similar.

ARMSTRONG, D.E.

1983

PRELIMINARY DRAFT OF PROJECT REPORT. PROJECT 807836010

MEMORANDUM TO MIKE MULLIN, PROJECT OFFICER, GROSSE ILE, MI: 36 P

The purpose of this memo is to provide a preliminary report of information to be contained in the final report on the project, "PCBs In Lake Michigan Tributaries, Waters, and Sediments". The final report will be presented in four sections: I. PCBs in Lake Michigan Tributaries, II. PCBs in Fish Samples from the Ashtabula and Fox Rivers. Part of the data from sections II and III has been transmitted previously. This memo focuses on the data on PCBs in Lake Michigan tributaries and lake water samples. Additional results from parts III and IV will be summarized in separate memos.

AUER, N.A. and M.T. AUER

1983

AN INVESTIGATION OF WALLEYE EGG HATCHING SUCCESS IN THE LOWER FOX RIVER, WISCONSIN

DRAFT, SUBMITTED TO E.P.A. GRANT R810076010, PROGRESS REPORT, DULUTH, MN: 33 P.

The walleye (Stizostedion vitreum) is endemic to Green Bay and the Fox River (Becker, 1983) and has been a part of the commercial and sport-fishing catch for many years. In 1885, the annual combined catch of pike and pickerel (walleye and northern pike) from lower Green Bay was 365,000 pounds (Smith and Snell, 1891). The walleye, however, has never been an abundant or highly sought-after component of the fishery in either the Fox River or lower Green Bay. Past commercial fishing operations in Green Bay have focused on lake trout (Salvelinus namaycush), whitefish (Coregonus clupeaformis), lake herring (Coregonus artedii), smelt (Osmerus mordax), and alewife (Alosa pseudoharengus). The most abundant catches of walleye have been associated with sport-fishing activities in northern Green Bay and Big- and Little Bay-De-Noc in the 1940s (Bertrand et al., 1976).

The Lower Fox River and southern Green Bay have, however, received some commercial fishing pressure. As late as 1973-74, walleye comprised 2.8-3.7% (by number) of the commercial catch at a site just downstream of the DePere Dam (Kernen, 1974). Analysis of data from commercial catch reports and Wisconsin Department of Natural Resources (WDNR) surveys, shows that walleye accounted for 3-15% of the catch in the Lower Fox River (fyke nets) and $\leq$1% of the catch in southern Green Bay (drop nets). While direct comparison is difficult due to differences in time and season of sampling and gear selectivity (fyke vs. drop nets), these data show that walleye are a relatively small component of the overall catch. The complete species composition breakdown for fyke net surveys in the Fox River for 1973-79 is presented.

BALL, J., F. PRIZNAR, and P. PETERMAN (COMPILERS)

1978

INVESTIGATION OF CHLORINATED AND NONCHLORINATED COMPOUNDS IN THE LOWER FOX RIVER WATERSHED

U.S. NTIS PB-292 818; GREAT LAKES NATL. PROGRAM, U.S. ENVIRON. PROT. AGENCY, CHICAGO, IL: 235 P.

This report concerns the existence, source and fate of chlorinated and non-chlorinated organic compounds in the Lower Fox River of Wisconsin. Raw and treated wastewaters, surface water, seston, snowmelt, sediment, fish and clams were sampled. A total of 105 compounds were identified and an additional 20 compounds were characterized by GC/MS. Twenty identified compounds are on the U.S. EPA Consent Decree Priority Pollutant List. The study shows PCBs and some other chloro-organics in effluents are reduced by efficient suspended solids removal. It is possible, but not proven, that some chloro-organics are formed by process or effluent chlorination. Clams were found to rapidly bio-accumulate PCBs. Fish fillet samples contained PCB concentrations up to 90 mg/kg. Sediments throughout most of the river were found to be contaminated with PCBs. An extensive bibliography is included.

BERGH, A.K. and R.S. PEOPLES

1977

DISTRIBUTION OF POLYCHLORINATED BIPHENYLS IN A MUNICIPAL WASTEWATER TREATMENT PLANT AND ENVIRONS

SCI. TOTAL ENVIRON. 8:197-204

Distribution of polychlorinated biphenyls (PCB) in sewage wastes at a municipal sewage treatment plant was studied, showing that the great bulk of PCBs entering such a treatment plant become adsorbed onto the grit chamber solids and the sludge that is passed from the anaerobic digesters. When appreciable quantities of PCBs are present in sewage, as was the case in this study, significant quantities can nevertheless pass with the effluents discharged from the treatment plant. The PCB concentrations in the treatment plant waters undergoing secondary and tertiary treatment tend to be consistent with the limited solubility properties of the PCBs. However, appreciably higher concentrations can be found in the sediments of waters receiving treatment plant discharges and bioaccumulation in fish is demonstrated readily. Also described are quantitative data on PCBs in soils fertilized with PCB-contaminated sludge.

BROWNLEE, B. and W.M.J. STRACHAN

1976

PERSISTENT ORGANIC COMPOUNDS FROM A PULP MILL IN A NEAR-SHORE FRESHWATER ENVIRONMENT

IN: L.H. KEITH (ED.), IDENTIFICATION & ANALYSIS OF ORGANIC POLLUTANTS IN WATER

ANN ARBOR SCI. PUBL. INC., ANN ARBOR, MI: 661-670

Our objective was to determine if any organic compounds present in the mill effluent could be detected at significant distances (up to 5 km) from the effluent outfall and therefore might be considered to be persistent. Procedurally this involved first, identifying as many constituents as possible in the mill effluent and second, determining if any of these compounds could be detected in water, seston or sediment samples taken according to a predetermined pattern of sampling sites. Conversely, those compounds which were not detectable outside the immediate mill area could be considered to be relatively nonpersistent.

Effluent plume movement was a major consideration as we were concerned primarily with compounds detectable outside the area influenced by the plume. Local reports were that predominant plume movement is in a southeasterly direction extending as far as Five Mile Point. This predominance was taken into account when the sampling pattern was chosen.

Fish tainting has been a problem for the commercial fishery in this area. Another study conducted at the same time as ours was directed toward the identification of suspect compounds in fish taken from the mill area. We hoped to be able to correlate our results with this study.

BROWNLEE, B. and W.M.J. STRACHAN

1977

DISTRIBUTION OF SOME ORGANIC COMPOUNDS IN THE RECEIVING WATERS OF A KRAFT PULP AND PAPER MILL

J. FISH. RES. BOARD CAN. 34:830-837

Water, seston, sediment, and macrophyte samples were collected from Nipigon Bay, Lake Superior at distances up to 6.8 km from the effluent discharge of a kraft pulp and paper mill at Red Rock, Ontario. Fifteen compounds have been identified in mill effluent and six of these were found in samples from the Bay. Mill-related compounds were found most often in water and sediment samples, less often in seston samples, and in none of the macrophytes samples. Dehydroabietic acid, present in mill effluent in excess of 1 mg/l, was found in most water and sediment samples and a few seston samples. This compound is a good indicator of the areal influence of the effluent. Palmitic acid and dioctyl phthalate were also widely distributed. Acetovanillone and sandaracopimaric acid were found in one water sample 1.0 km from the discharge. 7-oxodehydrobietic acid was found in five water samples at distances of up to 4.7 km from the discharge. This is apparently the first time that this compound has been reported in a mill effluent or in environmental samples.

BROWNLEE, B., M.E. FOX, W.M.J. STRACHAN, and S.R. JOSHI

1977

DISTRIBUTION OF DEHYDROABIETIC ACID IN SEDIMENTS ADJACENT TO A KRAFT PULP AND PAPER MILL

J. FISH. RES. BOARD CAN. 344:838-843

Sediments adjacent to a kraft pulp and paper mill on western Nipigon Bay, Lake Superior, were examined for resin acids. Dehydroabietic acid was the predominant resin acid with surficial concentrations of less than 5-100 ug/g.

The areal distribution indicated the mill to be the primary source of this compound. Depth profiles of the acid and core dating by ^{210}Pb methods enabled the calculation of a mean sediment accumulation rate of 0.11 cm yr^{-1} and a half-life for the disappearance of dehydroabietic acid in the sediments of approximately 21 yr. A half-life of 0.12 yr was estimated for this compound in the water column. It appears, therefore, that the primary removal mechanism of dehydroabietic acid is degradation in the water column.

BUELOW, C.R.

1982

ORGANICS IN THE LOWER FOX RIVER SYSTEM: SELECTED NEUTRAL COMPOUNDS

MS. THESIS, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

This study investigated the origin(s) of retene and related diterpene hydrocarbons in the Lower Fox River sediments. The following hypotheses were considered:

1. Retene and related compounds are generated from resin acid precursors during biotreatment of pulp and paper mill effluents.

2. Resin acids as precursors to retene are discharged to the river and are biodegraded in the sediments to intermediate hydrocarbons and retene.

3. Retene and related compounds are discharged to the river in pulp mill effluents as wood extractives, or in paper mill effluents as components of rosin size.

A second objective was to relate the distribution of retene in the sediments to the locations of discharges from pulp and paper mills or municipal wastewater treatment plants.

Objectives A and B required the adaptation and evaluation of analytical methods for the extraction and analysis of these compounds.

A minor objective was to describe the present distribution of polychlorinated biphenyls in the Lower Fox River sediments.

CAIRNS, M.A., A.V. NEBEKER, J.H. GAKSTATTER, and D.F. KRAWCZYK

1983

TOXICITY OF TWO WISCONSIN FRESHWATER SEDIMENTS TO INVERTEBRATES USING LIQUID (ELUTRIATE) AND SOLID PHASE BIOASSAYS

PRELIMINARY DRAFT, U.S. E.P.A., CORVALLIS, ENVIRON. RES. LAB, CORVALLIS, OR: 28 P.

Contaminated freshwater sediments from the Lower Fox River/Green Bay and the Phillips Lakes Chain, Wisconsin, were bioassayed for acute toxicity using Hyalella azteca, Gammarus lacustris, and Daphnia magna. D. magna were exposed for 48 hours and the two amphipods were exposed for 10 days to sediment and water in a 1:4 ratio in solid phase bioassays. D. magna were also exposed for 48 hours in liquid phase (elutriate) bioassays. The two most contaminated Green Bay/Fox River sediment samples caused highly significant ($\alpha = 0.01$) mortality in one of two liquid phase tests. The most contaminated sediment sample from the Phillips Lake Chain caused highly significant ($\alpha = 0.01$) mortality to H. azteca and D. magna and significant ($\alpha = 0.05$) mortality to G. lacustris in solid phase tests. The test organisms were sensitive and useful bioassay animals.

DAVIS, J.C.

1973

SUBLETHAL EFFECTS OF BLEACHED KRAFT PULP MILL ON RESPIRATION AND CIRCULATION IN SOCKEYE SALMON (ONCORHYNCHUS NERKA)

J. FISH. RES. BOARD CAN. 30(3):369-377

Sublethal effects of aerated neutralized, filtered, full bleach kraft mill effluent (BKME) on circulation and respiration of Pacific salmon were examined. Ventilatory water flow, oxygen uptake, cough frequency, and buccal pressure increased in a group of 19 sockeye salmon, Oncorhynchus nerka, 207-321 g, at 10.5 $\pm$ 0.5 C, upon initial exposure to sublethal BKME concentrations. The threshold concentration for these responses appeared to be around 20% of the 4 day LC50 (static bioassay).

Following overnight exposure to BKME, ventilatory volume, oxygen uptake rate, cough frequency, and oxygen utilization tended to approach pre-exposure levels, particularly at the higher sublethal contractions. Changing effluent toxicity, acclimation phenomena, or physiological adjustment are discussed as possible explanations for these results.

Measures of arterial oxygen tension in sockeye salmon indicated that arterial tension declines rapidly and remains depressed following up to 24 hour exposure to BKME (33-47% of 4 day LC50). On the average this decline represented a 20% decrease in oxygen saturation of the blood. Decreased arterial PO_2 may be due to mucous production at the gills and resulting gas diffusion problems, as well as abnormalities in ventilation. Reduction in scope for activity might result from impaired oxygen uptake at the gills. A similar response was observed in rainbow trout, salmo airdneri.

DELFINO, J.J. and D.B. EASTY

1979

INTERLABORATORY STUDY OF THE DETERMINATION OF POLYCHLORINATED BIPHENYLS IN A PAPER MILL EFFLUENT

ANAL. CHEM. 51(13):2235-2239

Six laboratories collaboratively studied a method for determining polychlorinated biphenyls (PCBs) in paper mill effluent. In preliminary studies, the recovery and relative standard deviation (RSD) for the PCB Aroclor 1242 added to and extracted from distilled water were 95.6% and 14.7%, respectively. Because the RSD of data from direct injection of Aroclor 1242 solutions into the gas chromatograph was of similar magnitude, 15.6%, gas chromatographic analysis appeared to provide the principal source of variation in the overall determination. Participating laboratories achieved an average 93.7% recovery of Aroclor 1242 added to a paper mill effluent: their data had a RSD of 16.0%. The results indicate that the method is satisfactory for use with paper mill effluents having PCB concentrations above 2 ug/L and it compares favorably with findings from studies in other environmental matrices. Greater variation might be expected from effluents containing significant interferences.

DELLINGER, R.W.

1980

DEVELOPMENT DOCUMENT FOR PROPOSED EFFLUENT LIMITATIONS GUIDELINES AND STANDARDS FOR THE PULP, PAPER AND PAPERBOARD AND THE BUILDERS' PAPER AND ...

OFFICE WATER WASTE MANAGE., EPA 440/1-80/025-B, U.S. EPA, WASHINGTON, DC.; U.S. NTIS PB81-201535: 634 P.

This document presents the findings of a study of the Pulp, Paper, and Paperboard and the Builders' Paper and Board Mills Point Source Categories for the purpose of developing effluent limitations guidelines for existing and new point sources and to establish pretreatment standards for existing and new dischargers to publicly owned treatment works to implement Sections 301, 304, 306, 307, 308, and 501 of the Clean Water Act (the Federal Water Pollution Control Act Amendments of 1972, 33 USC 1251 et seq., as amended by the Clean Water Act of 1977, P.L. 95-217 (the "Act";).

The information presented in this document supports regulations proposed in December 1980. Information is presented to support best available technology economically achievable (BAT) best convertional pollutant control technology (BCT), new source performance standards (NSPS), pretreatment standards for new and existing sources (PSNS and PSES) for the Pulp, Paper, and Paperboard and the Builders' Paper and Board Mills Point Source Categories. The report presents and discusses data gathering efforts, subcategorization, water use, pollutant parameters, control and treatment technologies, development of regulatory options, cost and non-water quality considerations, and the methodology for development of effluent limitations.

DOSKEY, P.V. and A.W. ANDREN

1981

MODELING THE FLUX OF ATMOSPHERIC POLYCHLORINATED BIPHENYLS ACROSS THE AIR/WASTE INTERFACE

ENVIRON. SCI. TECHNOL. 15(6):705-711

Problems involved in measuring and modeling polychlorinated biphenyl (PCB) fluxes across the air/water interface are addressed. Speciation of airborne PCBs, operationally defined by partitioning through a glass-fiber filter, indicate that greater than 90% exist in the vapor phase. Indirect calculations based on semiempirical expressions predict that particlebound Aroclors are primarily associated with submicrometer-size aerosols. Mono- and dichlorobiphenyl vapor is collected poorly by available collection methodologies. Quantification of environmental samples is further complicated by weathering of individual Aroclor components. A model of the PCB flux across the air/water interface, employing Lake Michigan as an example, is presented which includes the processes of vapor and particle deposition, volatilization, and bubble ejection. The importance of vapor deposition and volatilization is dependent upon the magnitude of the Henry's law constant derived from laboratory and environmental data are used to elucidate the flux of atmospheric PCBs to Lake Michigan.

ELLIS, R.H.

1967

EFFECTS OF KRAFT PULP MILL EFFLUENT ON THE PRODUCTION AND FOOD RELATIONS OF JUVENILE CHINOOK SALMON IN LABORATORY STREAMS

TECHNICAL BULL. NO. 210, NATIONAL COUNCIL FOR STREAM IMPROVEMENT, INC: 55 P.

The effects of kraft pulp mill effluent (KME) on the growth, production, and food consumption of juvenile chinook salmon, Oncorhynchus tschawytscha (Walbaum), and on the abundance of their food organisms were studied in simplified communities in six laboratory streams. The investigation was conducted between June 1966 and June 1967 at the Pacific Cooperative Water Pollution and Fisheries Research Laboratory, Oregon State University.

The waste, which was collected weekly from settling lagoons of a kraft pulp mill producing paper from unbleached pulp, was introduced into the laboratory streams at a constant flow rate. The toxicity of each batch of waste was characterized by acute toxicity bioassays for which 96-hour median tolerance limit (TL_m) values were established. The concentration of acutely toxic substances added to each stream was expressed as a decimal fraction of the TL_m values.

Salmon growth rate and production were reduced in laboratory streams that received KME at a concentration of 15 ml/liter (1:67 dilution) and a toxicity ranging from 0.14 to 0.36 TL_m. Little or no reduction was found to occur in streams that received waste at a concentration of 5 ml/liter (1:200 dilution) and a toxicity ranging from 0.05 to 0.08 TL_m. The reductions in growth rate and production in the 15 ml/liter streams were greater at high stocking densities than at low stocking densities. With the exception of the highest stocking levels, food consumption was usually as high in the 15 ml/liter streams as in the control or 5 ml/liter streams. Estimates of food abundance in the laboratory streams did not indicate any reduction attributable to the waste.

The reductions in growth rate and production at concentrations of 15 ml/liter were attributed to a direct toxic effect of the waste. Information on the food abundance, food consumption, and activity of the salmon at the highest stocking densities indicated that the waste was affecting either the desire or the ability of the salmon to feed. The interaction between salmon stocking density and KME toxicity indicates the need for understanding the influence of other environmental factors in studies of the effect of kraft pulp mill effluents on fishery resources.

EPSTEIN, E., M. BRYANS, D. MEZEI, AND D. PATTERSON

1974

LOWER GREEN BAY: AN EVALUATION OF EXISTING AND HISTORICAL CONDITIONS

U.S NTIS PB-236 414; EPA CONTRACT NO. 68-01-1572,
REGION V, U.S. ENVIRON. PROT. AGENCY: 281 P.

A survey is made of current and historical information relating to the quality of the waters of Green Bay, Lake Michigan. The steady decline in water quality over the last four decades is documented. A historical shift in fish production from high quality native species to low quality exotic species has occurred. Increasing areas of the Bay exhibit low oxygen levels. In winter, under the ice, low oxygen levels now extend into the Bay as far as 40 kilometers. Nutrient loads have caused the areas where eutrophic conditions exist to increase. These and other factors have led to a dislocation of recreational use.

Documentation of the expected reduction in pollutant loads due to present control strategies is also provided. Field studies performed in this program indicate slight improvements in Bay water quality over recent years. A water quality model, suitable for winter conditions, is also being developed which will allow predictions of improvement in Bay water quality due to present and future pollution control strategies. The final report will be available in January, 1975.

FOX, M.E.

1976

FATE OF SELECTED ORGANIC COMPOUNDS IN THE DISCHARGE OF
KRAFT PAPER MILLS INTO LAKE SUPERIOR

IN: L.J. KEITH (ED.), IDENTIFICATION & ANALYSIS OF ORGANIC POLLUTANTS IN WATER

ANN ARBOR SCI. PUBL. INC., ANN ARBOR, MI: 641-659

In 1973, studies on pulp mill wastewater discharges on Lake Superior were initiated by the International Joint Commission, Upper Lakes Reference Group. This group had the task of reporting to the International Joint Commission (IJC) on the impact of point source effluent discharges on the basically high-quality receiving waters of the Upper Great Lakes (Huron and Superior). Apart from domestic sewage, pulp and paper mill effluents constitute the major polluting discharges into the Upper Great Lakes. Pulp and paper mill effluents have been implicated in oxygen depletion, toxicity and production of taste and odor problems in the receiving water and its aquatic communities.

The studies initiated were wide-ranging in scope and included many projects in the chemical, physical and biological fields. This chapter will report on the findings of one of those projects. Its object was to determine the fate and effective zone of persistence of dissolved organic compounds in the effluent plume.

FOX, M.E.

1977

PERSISTENCE OF DISSOLVED ORGANIC COMPOUNDS IN KRAFT PULP AND PAPER MILL EFFLUENT PLUMES

J. FISH. RES. BOARD CAN. 34:798-804

The persistence of dissolved organic compounds in the effluent plumes of a pulp and paper mill on the north shore of Lake Superior was studied in 1974. Approximately 90 organic compounds were observed of which 36 (including all the major ones) were identified.

The dispersion of five of these compounds was examined quantitatively. Dehydroabietic acid was the only major organic compound observed to exhibit measurable persistence >2000 m from the effluent discharge. At 2000 m from the discharge, levels of 30 ug/l dehydroabietic acid were detected within the plume and 15 ug/l outside the effluent plume. The disappearance of dehydroabietic acid parallels that of the conservative ion Na^+, indicating dilution by the receiving water as the only significant short-term removal mechanism.

FOX, M.E., D.M. WHITTLE, and K.L.E. KAISER

1977

DEHYDROABIETIC ACID ACCUMULATION BY RAINBOW TROUT (SALMO GAIRDNERI) EXPOSED TO KRAFT MILL EFFLUENT

J. GREAT LAKES RES. 3(1-2):155-158

Rainbow trout (Salmo gairdneri) were examined for the presence of dehydroabietic acid after exposure to kraft mill effluent. Levels of 2 to 10 ug/g dehydroabietic acid on a whole fish wet weight basis were found in fish exposed to 3 to 18% effluent for 48 to 144 hours. Less than 1 ug/g dehydroabietic acid was found in control fish which had been acclimated in Nipigon Bay water for two weeks and no residue was detected in an unexposed fish. It is concluded that fish exposed to kraft mill effluent accumulate dehydroabietic acid to a level which is likely to result in sublethal toxic effects.

FUJIYA, M.

1961

EFFECTS OF KRAFT PULP MILL WASTES ON FISH

J. WATER POLLUT. CONTROL FED. 33(9):968-977

In recent years, the many pulp mills built in Japan have been the source of serious liquid waste problems. As a result, extensive and intensive studies have been carried out to determine the effects of these wastes on fish, shellfish, seaweed, and other aquatic organisms from various points of view.

Among the studies carried out have been ecological researches on the lethal dose, avoidance reaction, and others. Physiological studies by the paper electrophoretic method of serum separation had already been performed on fish. On the other hand, the effects on the activity of seaweeds for phosphorus assimilation and the calcium absorption by shellfish had been studied, and discussed physiologically. Although satisfactory results were obtained from these, a histo-pathological approach also would be necessary for investigating the effects on fish. Therefore, a cyto-chemical experiment was inaugurated to study the histo-pathological effect on fish exposed in the water influenced by the waste. It was deemed important to determine the toxicity of the waste to fish.

JAMES E. GROOSE

1982

ORGANICS IN THE LOWER FOX RIVER SYSTEM: SELECTED ACIDIC COMPOUNDS

MS. THESIS, UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

The overall goal of this thesis was to determine the extent of contamination in the Lower Fox River and lower Green Bay due to certain acidic organic compounds.

This goal was approached by considering five specific objectives:

1. To perform a literature review of selected acidic organic compounds related to pulp and paper mill activities;

2. To optimize the methodology for extraction, derivatization and analysis of selected acidic organic compounds;

3. To quantify the concentrations of selected compounds in wastewaters discharged to, and present in, river water and sediments of the Lower Fox River system:

4. To determine sources and sinks for selected organic compounds; and

5. To generate a "limited mass balance" for selected acidic organic compounds through a municipal wastewater treatment plant and an integrated pulp and paper mill.

HICKEY, J.J., J.A. KEITH, and F.B. COON

1966

AN EXPLORATION OF PESTICIDES IN A LAKE MICHIGAN ECOSYSTEM

J. APPL. ECOL. 3 (SUPPL):141-153

The primary purpose of this study has been to determine what pesticide residues, if any, are present at different trophic levels in a Lake Michigan ecosystem with particular reference to the Green Bay area. Our main findings of this exploratory study are summarized in the present report. A secondary purpose, contingent upon the finding of DDT contamination, involved an attempt to understand the biological significance, if any, of pesticide residues encountered in various layers of the Lake Michigan animal pyramid. The research strategy behind this project was a direct development of the concept of ecological concentration of a pesticide in an aquatic ecosystem. The second strategic element was the concept of pesticide transport by soil particles.

W.D. JOHNSON, F.D. FULLER and L.E. SCARCE

1967

PESTICIDES IN THE GREEN BAY AREA

PROCEEDINGS, TENTH CONFERENCE ON GREAT LAKES RESEARCH, 1967

Pesticides in man's environment are being studied with increasing intensity and interest because of the rapid increase in their usage in agriculture. As national concern has increased, several of the Federal Water Pollution Control Administration laboratories were equipped to analyze samples from the aqueous biosphere. As part of this Federal effort, the Great Lakes-Illinois River Basins Project initiated pilot studies to investigate the effects of pesticides on the aqueous environment of Green Bay. The areas studied were Door County, located at the northerly end of Green Bay Peninsula, and tributaries on the western, southern and northern shores of Green Bay.

This paper describes analytical methods used, type of samples analyzed, and concentration of the various common chlorinated pesticides detected. The significance and effects of these compounds at the observed levels are discussed, relative to their toxic effects on the aquatic environment and man.

KEITH, L. H.

1975

ANALYSIS OF ORGANIC COMPOUNDS IN TWO KRAFT MILL WASTEWATERS

ENVIRON. MONITOR. SER. EPA-600/4-75-005,
U.S. EPA, CORVALLIS, OR: US. NTIS PB247 698: 99 P.

Wastewaters from two kraft paper mills in Georgia were sampled at various points in the waste treatment systems. Gas chromatography of the organic extracts and identification of many of the specific chemical components by gas chromatography-mass spectrometry provided a "chemical profile" of the effluents. The mills, in different geographical locations, have very similar raw wastewater compositions but different effluents are qualitatively similar in composition although the quantities of the various components differ. After two years the raw and treated effluents of both mills were re-sampled. Analyses showed that although concentrations of the organics varied, the same compounds are still present.

KERNEN, L.T.

FISHERY INVESTIGATIONS ON THE LOWER FOX RIVER AND
SOUTH GREEN BAY IN 1973-1974

WISCONSIN DEPT. NATURAL RESOURC., MEMO

Fish populations in the Fox River and South Green Bay were investigated through the use of three types of gear, with emphasis on the two and one-half mile section of the Fox River downstream from the DePere Dam. Data was collected by monitoring commercial net lifts, electro-fishing, and shoreline seining. In the Fox River, 45 fish species were recorded with bullhead spp., carp, white bass, and white sucker accounting for approximately 80% by number of 23,202 fish examined over the two-year period. A total of 32 species of fish were identified from Green Bay, with yellow perch, alewife, bullhead spp., burbot, and white sucker comprising 90% by number in 1973 and 98% in 1974 of a 182,852 fish sample.

KINAE, N., T. HASHIZUME, T. MAKITA, I. TOMITA, I. KIMURA, and H. KANAMORI

1981 A

STUDIES ON THE TOXICITY OF PULP AND PAPER MILL EFFLUENTS - I. MUTAGENICITY OF THE SEDIMENT SAMPLES DERIVED FROM KRAFT PAPER MILLS

WATER RES. 15:17-24

Sediment samples collected at three different coastal points (Shinguu, Ooigawa and Tagonoura) were extracted with diethylether and then methanol. Each extract was separated into five fractions by high-speed liquid chromatography and they were submitted to mutagenic assay using B. subtilis and S. typhimurium and to GC-MS analysis.

The ether fraction of sediment sample from Shinguu showed DNA damaging potency on B. subtilis and exhibited mutagenic effect on S. typhimurium TA 98, TA 100 and TA 1537. 2,4,6-Trichlorophenol, 3,4,5,6-tetrachloroguaiacol, dehydroabietic acid, pyrene and fluoranthene were mutagenic substances among 28 substances identified and tested.

KINAE, N., T. HASHIZUME, T. MAKITA, I. TOMITA, I. KIMURA, and H. KANAMORI

1981 B

STUDIES ON THE TOXICITY OF PULP AND PAPER MILL EFFLUENTS- II. MUTAGENICITY OF THE EXTRACTS OF THE LIVER FROM SPOTTED SEA TROUT (NIBEA MITSUKURII)

WATER RES. 15:25-30

The liver samples of spotted sea trout (Nibea mitsukurii) caught in three different coastal waters of Japan were extracted with diethylether and then methanol. The extracts were submitted to mutagenic assay using Bacillus subtilis and Ames strains of Salmonella typhimurium. The ether extract of the liver was found to have DNA damaging potency on B. subtilis. The extract was applied to a high-speed liquid chromatography to separate into five fractions and each was tested for the mutagenic effects. The fraction of HLC-9 showed DNA damaging and mutagenic potency on B. subtilis and S. typhimurium TA 98 respectively. Gaschromatographic-mass spectrometric examination of each fraction revealed 18 organic compounds of which 12 substances were identical with those found in the sediment samples. 9,10-Epoxystearic acid was mutagenically active among them.

LANDNER, L., K. LINDSTROM, M. KARLSSON, J. NORDIN, and L. SORENSEN

1977

BIOACCUMULATION IN FISH OF CHLORINATED PHENOLS FROM KRAFT PULP MILL BLEACHERY EFFLUENTS

BULL. ENVIRON. CONTAM. TOXICOL. 18(6):663-673

The present work is an attempt to find out if the low-molecular chlorinated compounds, identified to be present in low concentration in the effluents from Swedish kraft pulp bleacheries and some of which have been shown to be acute-toxic to fish, furthermore show tendencies to accumulate in fish. If such a bioaccumulation is demonstrated to occur, this would be a strong rationale for further studies on possible long term or chronic effects of this group of compounds.

LEACH, J.M. and L.T.K. CHUNG

1980

DEVELOPMENT OF A CHEMICAL TOXICITY ASSAY FOR PULP MILL EFFLUENTS

EPA-600/2-80-206, U.S. EPA, CINCINNATI, OH: 96 P.

A chemical analysis procedure was developed to measure, within 1.5 hours, compounds responsible for the toxicity of pulp mill effluents to fish. Analytical results for 113 samples of raw and biologically-treated bleached and unbleached kraft, sulphite and groundwood effluents were converted via toxic units into estimates of acute lethal toxicity. Agreement between 96-h medial lethal concentrations calculated by this method, and values from bioassays of the effluents using rainbow trout was within 30% for 73% of the samples examined.

Biological treatment was highly effective in removing the known toxic compounds at pulp mills on the Willamette River, OR. and the Androscoggin River, N.H. and ME., based on estimates of toxicant loadings into and out of the biobasins.

LEACH, J.M. and A.N. THAKORE

1973

IDENTIFICATION OF THE CONSTITUENTS OF KRAFT PULPING EFFLUENT THAT ARE TOXIC TO JUVENILE COHO SALMON (ONCORHYNCHUS KISUTCH)

J. FISH. RES. BOARD CAN. 30(4):479-484

The nonvolatile constituents that are acutely toxic to juvenile coho salmon (Oncorhynchus kisutch) have been fully identified in a kraft pulping effluent derived from Douglas fir and western hemlock. Toxicity and material balances were maintained throughout a fractionation procedure leading to isolation of the toxic factors.

Over 80% of the toxicity was caused by three resin acid soaps: sodium isopimarate (55%), sodium abietate (22%), and sodium dehydroabietate (5%). The remaining toxicity (18%) was contributed by sodium salts of the unsaturated fatty acids: palmitoleic, oleic, linoleic, and linolenic.

LEACH, J.M. and A.N. THAKORE

1975

ISOLATION AND IDENTIFICATION OF CONSTITUENTS TOXIC TO JUVENILE RAINBOW TROUT (SALMO GAIRDNERI) IN CAUSTIC EXTRACTION EFFLUENTS FROM KRAFT PULPMILL...

J. FISH. RES. BOARD CAN. 32:1249-1257

Chemical constituents in effluent from the caustic extraction stage of the bleach plant at a western Canada kraft pulpmill were fractionated to identify factors responsible for their toxicity to juvenile rainbow trout (Salmo gairdneri). At all stages in the fractionation procedure bioassays were carried out to monitor toxicities of the isolated materials. Five toxic compounds, separated in a pure state from the effluent, were characterized by chromatography, spectroscopy, and chemical synthesis. The compounds and their 96-h median lethal concentrations (LC50) measured in static bioassays were: 3,4,5-trichloroguaiacol (0.75 mg/liter), 3,4,5,6-tetrachloroguaiacol (0.32 mg/liter), monochlorodehydroabietic acid (0.6 mg/liter), dichlorodehydroabietic acid (0.6 mg/liter), 9,10-epoxystearic acid (1.5 mg/liter).

The same compounds were shown to be present in caustic extraction effluents collected from six other western kraft mills. For two samples, the concentration - toxicity graphs from bioassays of solutions containing only the pure toxicants in the amounts found by analysis were similar to those of the actual effluents produced by the mills. Concentrations of the toxic constituents in samples from six different mills were equivalent to 2.3-24 TU (toxic units), confirming that they are important factors in the toxicity of caustic extraction effluents.

LEACH, J.M. and A.N. THAKORE

1976

TOXIC CONSTITUENTS IN MECHANICAL PULPING EFFLUENTS

TAPPI 59 (2):129-132

Constituents toxic to fish were identified in mechanical pulping effluents from mills operating on mixtures of spruce (75-85%), pine (15-25%), and fir (5%). Chemical fractions separated from effluent samples were monitored for toxicity to juvenile rainbow trout throughout stages of a fractionation procedure based on chromatographic techniques. Individual toxic compounds were identified by comparison of their spectroscopic characteristics with those of chemically synthesized materials. Acute toxicities of pure samples of the identified compounds were measured in bioassays using rainbow trout. The predominant toxicants were the resin acids, isopimaric, palustric, dehydroabietic, abietic, pimaric, sandaracopimaric and neoabietic, which together accounted for 60-90% of overall toxicity in the mechanical pulping effluents studied. Minor toxic factors included alcohols related to the above acids, in particular pimarol and isopimarol, and an insect growth regulator, juvabione, and some of its derivatives. Other potentially toxic compounds included diterpene aldehydes, unsaturated fatty acids, and (epi)manool. Total resin acid concentrations in mechanical pulping effluents, measured by gas chromatography, ranged from 12-62 mg/liter, whereas median lethal concentrations (96-hr LC50) of these compounds for juvenile rainbow trout were 0.4-1.1 mg/liter in static bioassays. Resin acids were also present in effluent samples that were only partly detoxified by biological treatment.

LEACH, J.M. and A.N. THAKORE

1977

COMPOUNDS TOXIC TO FISH IN PULP MILL WASTE STREAMS

PROG. WAT. TECH. 9:787-798

The major toxic factors in effluents from Canadian softwood kraft, sulphite and mechanical pulping operations, and in wood debarking effluents, were seven resin acids; dehydroabietic, abietic, isopimaric, palustric, pimaric, sandaracopimaric, and neoabietic. Median lethal concentrations (96-h LC50) of the pure compounds for juvenile coho salmon (Oncorhynchus kisutch) were 0.2 - 0.8 mg 1^{-1} in bioassays with solution replacement every 4 - 8 h. Pulping and debarking effluents frequently contained resin acids at levels equivalent to 100 toxic units. The long-chain unsaturated fatty acids, oleic, linoleic, linolenic and palmitoleic also contributed to the toxicity of these waste streams.

In mechanical pulping effluents, minor toxic factors included the diterpene alcohols, pimarol and isopimarol, (96-h LC50, 0.3 mg 1^{-1}), and several naturally occurring insect juvenile hormone mimics related to juvabione (96-h LC50, 0.8 - 2.0 mg 1^{-1}).

A completely different group of compounds was responsbile for the toxicity of effluents from pulp bleaching plants. A major toxic factor in chlorination-stage bleaching effluent was identified as chlorolignin. In caustic extraction effluents, the predominant toxic contributors were trichloro- and tetrachloroguaiacol, monochloro-and dichloro- dehydroabietic acid, (96-h LC50, 0.3 - 0.75 mg 1^{-1}), and 9, 10-epoxy- and 9,10-dichloro- stearic acid (96-h LC50, 1.5 and 2.5 mg 1^{-1}, respectively). Pitch dispersant additives were also implicated as minor toxic factors in some caustic extraction effluents.

Contributions of the identified materials to effluent toxicity are described in terms of the toxic units concept. The toxicants are discussed in relation to their origin, to effluent discharge regulations, and to the choice of effluent treatment techniques.

LEACH, J.M., J.C. MUELLER, and C.C. WALDEN

1976

IDENTIFICATION AND REMOVAL OF TOXIC MATERIALS FROM KRAFT AND GROUNDWOOD PULP MILL EFFLUENT

PROCESS BIOCHEM. 11 (1):7-10

Pulp and paper mills discharge large volumes of effluent that can be detrimental to aquatic fauna in receiving waters. In many countries regulations exist limiting the suspended solids content, biochemical oxygen demand and in some cases the color of pulp mill effluents. Federal and Provincial Government regulations in Canada are additionally concerned with the toxicity to fish of pulp mill wastes. Efforts have been made to identify the nature and sources of toxic materials in effluents from paper pulp manufacture and to improve detoxification techniques. Recent progress in these areas relative to kraft and goundwood mill effluents is summarized in this article.

LEUNG, P. - S.K. and N.J. SELL

1982

EFFECT OF THE PAPER INDUSTRY ON WATER QUALITY OF THE LOWER FOX RIVER

WATER RESOUR. BULL. 18(3): 495-502

The Lower Fox River, Wisconsin, hosts the densest concentration of paper mills in the U.S., with 18 located along a 40-mile stretch between Lake Winnebago and Green Bay, Lake Michigan. Some of these companies use only primary, others also secondary, waste treatment techniques. Comparison of the quantities of wastes discharged with the legal limits indicates that all plants discharge only 40-50 percent or less of the allowable suspended solids; most discharge <50 percent of the allowable BOD. This is equal or better than the performance of paper companies elsewhere in the state. Reductions in pollutant discharges have corresponded to improved water quality, though too much BOD is still discharged to be adequately assimilated by the Fox River. The relatively low current level of discharges means permit levels would have to be drastically cut to make any significant impact on water quality. Only a few companies might be seriously affected by such changes. Flow and temperature related permits would likely be more effective, but more difficult to comply with for the industry. Toxic substances are also a potential problem, particularly chlororganic compounds that can form *in situ* from the chlorine frequently used for pulp bleaching.

LINKO, R.R., P. RANTAMAKI, and K. URPO

1974

PCB RESIDUES IN PLANKTON AND SEDIMENT IN THE SOUTHWESTERN COAST OF FINLAND

BULL. ENVIRON. CONTAM. TOXICOL. 12(6):733-738

The purpose of this study was to determine residues of PCBs in the plankton from the Turku Archipelago off the southwestern coast of Finland. Preliminary experiments were also made to find PCBs absorbed into the sediment.

NATIONAL COUNCIL OF THE PAPER INDUSTRY FOR AIR AND STREAM IMPROVEMENT

1982

EFFECTS OF BIOLOGICALLY STABILIZED BLEACHED KRAFT MILL EFFLUENT ON COLD WATER STREAM PRODUCTIVITY AS DETERMINED IN EXPERIMENTAL STREAMS- FIRST ...

TECH. REPT. NO. 368, NCASI, NEW YORK, NY: 66 P.

This technical bulletin presents the results of the first years' effluent study in which two controlled streams received 0.5 ppm BOD addition of biologically treated bleached results of increasing effluent concentrate additions. Separate reports will be developed after several years of stream study to provide a comprehensive discussion of cummulative knowledge developed relative to fish production and other components of the food web (benthic and algal production).

NG, K.S., J.C. MUELLER, AND C.C. WALDEN

1974

PROCESS PARAMETERS OF FOAM DETOXIFICATION OF KRAFT EFFLUENT

PULP PAPER MAGAZINE CAN. 75(7) : 101-106

This study has been directed to assess the effective range of process variables for detoxification and to investigate the possiblity of reducing the treatment time from the 24-hr reuiqred previously. Optimum conditions were used to develop a continuous system and the beneficial effects under normal operating conditions were examined. Based on the findings, preliminary cost estimates have been made for the foam separation process.

MARY E. PARISO, JAMES R. ST. AMANT, AND THOMAS B. SHEFFY

1984

MICROCONTAMINANTS IN WISCONSIN'S COASTAL ZONE

IN TOXIC CONTAMINANTS IN THE GREAT LAKES, ED.: J.O. NRIAGU AND M.S. SIMMONS,

JOHN WILEY AND SONS, NEW YORK

Microcontaminants were identified in Wisconsin's coastal zone almost 20 years ago. Fourteen studies conducted between 1965 and 1979 provide a partial record of these microcontaminants. A subsequent three-year study conducted by the Wisconsin Department of Natural Resources compiles a complete and up-to-date inventory of microcontaminants in Wisconsin's coastal zone.

In 1979, problem drainage systems were identified using fish as a biological indicator. The results of this survey showed that of the 16 toxic substances monitored, only four represented problems for Wisconsin's coastal zone: PCB, DDT, chlordane, and dieldrin. PCB was found to be the worst contaminant statewide. Fish tested from Lake Superior and its tributary streams showed that the quality of fish from this basin is high. Fish from Lake Michigan and its tributary streams were found to contain varying levels of PCB, chlordane, DDT, and dieldrin.

In 1980, intensive sampling of problem areas identified in the first year survey defined more precisely the limits and potential sources of contamination. Fish and sediment data indicated that a PCB problem persists in specific areas of the following drainage systems: Sheboygan River, Milwaukee River, Kinnickinnic River, Menomonee River, Pike River, Root River, and Fox River. Mass spectrometry analysis of selected fish tissue samples identified the presence of a variety of compounds that had not been monitored before.

In 1981, fish, sediment, and effluent monitoring continued for the purpose of evaluating trends in contaminant levels and continuing the effort to identify and eliminate point sources of toxic substances. PCB problem areas were again found in the Fox, Milwaukee, Kinnickinnic and Pike Rivers.

PATTERSON, D.

1980

WATER QUALITY MODELLING OF THE LOWER FOX RIVER FOR WASTELOAD ALLOCATION DEVELOPMENT

WISCONSIN DEPT. NATURAL RESOUR., BUREAU WATER QUAL.: 90 P.

The Fox River from Lake Winnebago to the DePere Dam was modelled using a finite difference water quality model. The QUAL model was adopted and extensively modified by the Wisconsin DNR staff which used the QUAL II model as a starting point for model development. The final model simulates dissolved oxygen, two terms of BOD, total phosphorous, organic nitrogen, ammonia, nitrate, chlorophyll-a and sediment oxygen demand. The model can be run in both the steady state and dynamic mode.

The QUAL III model as developed was successfully calibrated for eleven separate synoptic water quality surveys and verified with nine dynamic runs that each covered a minimum of 27 days of simulation. The surveys covered the years 1972 to 1979 and generally fell in the annual low flow high temperature period. Wasteload allocations (WLAs) have been developed for the several dischargers on this river segment based on the models results.

PETERMAN, P.H., J.J. DELFINO, D.J. DUBE, T.A. GIBSON, and F.J. PRIZNAR

1980

CHLORO-ORGANIC COMPOUNDS IN THE LOWER FOX RIVER, WISCONSIN

IN: B.K. AFGHAN AND D. MACKAY (EDS.), HYDROCARBONS AND HALOGENATED HYDROCARBONS IN THE AQUATIC ENVIRONMENT, PLENUM PRESS, NEW YORK: 145-160

The Lower Fox River, Wisconsin is one of the most densely developed industrial river basins in the world. During 1976-1977 about 250 samples were analyzed by GC and GC/MS including biota, sediments, river water and wastewaters from 15 pulp and/or paper mills and 12 sewage treatment plants. A total of 105 compounds were identified in selected extracts by GC/MS with another 20 compounds characterized but not conclusively identified. Twenty of the 105 compounds are on the EPA Priority Pollutant List. Other compounds identified in pulp and paper mill wastewaters, including chloroguaiacols, chlorophenols, resin acids and chloro-resin acids have been reported toxic to fish by other investigators. Several compounds apparently not previously reported in wastewaters are chloro-syringaldehyde, chloroindole, trichlorodimethoxyphenol, and various 1-4 chlorinated isomers of bisphenol A. Concentrations of the various compounds, when present in final effluents, ranged from 0.5 to ca. 100 ug/L. An exception was dehydroabietic acid, a toxic resin acid not found on the EPA Priority Pollutant List. It was frequently found in pulp and paper mill effluents in concentrations ranging from 100 to 8500 ug/L. PCBs were found in all of the matrices sampled. Sixteen of the 35 fish exceeded the FDA limit of 5 mg/kg, while 31 of the 35 exceeded the Canadian limit of 2 mg/kg. Concentrations of PCBs and other chloro-organics were related to point source discharges. There was a direct correlation of the concentrations of these compounds in wastewater with suspended solids values.

SAGER, P.E. AND J.H. WIERSMA

1972

NUTRIENT DISCHARGES TO GREEN BAY, LAKE MICHIGAN FROM THE LOWER FOX RIVER

PROC. 15TH CONF. GREAT LAKES RES.:132-148

Seasonal variations in discharge of nutrients and organic matter from the Fox River to Green Bay were related to the quality of Lake Winnebago discharges and to processes of assimilation sedimentation and release in the river. Lake Winnebago's effects on the river included increased levels of ammonia-nitrogen in spring, total phosphate in summer and orthophosphate in fall.

Anoxic conditions in portions of the river indicate excessive organic loading and are significant in ammonia-nitrogen releases. Phosphate assimilation in the river is evident from decreases in loadings between Lake Winnebago and Green Bay in summer and fall. Maximum loadings of phosphates and organics during winter and spring reflect high flows, reduced assimiliation and releases from the drainage system.

Annual average loadings of orthophosphate and total phosphate from municipal treatment plants were 4400 and 6670 lb/day, respectively. Discharges from Lake Winnebago included annual average loadings of 2070 and 6620 lb/day of orthophosphate and total phosphate, respectively. Annual average loading of ammonia-nitrogen from treatment plants was 4440 lb/day and from Lake Winnebago 5200 lb/day.

At the mouth of the river, annual average loadings to Green Bay in lb/day included 3080 for orthophosphate, 13,200 for total phosphate, 17,100 for nitrate-nitrogen and 12,400 for ammonia-nitrogen.

SERVIZI, J.A.

1974

TOXICITY TO AQUATIC ORGANISMS CAUSED BY CHLORINATION

PROC. BRITISH COLUMBIA WATER WASTE ASSOC.,
VANCOUVER, B.C., CANADA:172-182

Field and laboratory studies have demonstrated that chlorinated municipal sewage is highly toxic to fish and in some cases disrupts natural migration and species distribution. In each case, the principal source of toxicity was chlorine applied during disinfection, which increased toxicity of primary and secondary effluents by several fold. However, in the absence of chlorine, primary effluents were toxic, while effluents from the secondary treatment process were virtually nontoxic.

Chlorinated municipal sewage typically has a combined available chlorine residual which may vary from 0.1 mg/l to several times this value and the optimum residual may be 3 to 4 mg/l measured amperometrically. On the other hand, information presented herein indicates that acute toxicity or sublethal toxic conditions for fish are likely when chlorine residuals exceed 0.02 mg/l. Therefore, the major step in obtaining a nonlethal treated municipal sewage is limitation of chlorine residual to less than 0.02 mg/l chlorine in the effluent, measured amperometrically. In addition to limiting chlorine residual, acute toxicity of municipal sewage can be reduced to virtually nil if it undergoes secondary treatment. These objectives can be attained using known technology and principles and without jeopardizing public health or other water uses.

SERVIZI, J.A. and R.W. GORDON

1973

DETOXIFICATION OF KRAFT PULP MILL EFFLUENT BY AN AERATED LAGOON

PULP PAPER MAGAZINE CAN. 74(9):103-110

An 8-month study of the aerated lagoon at Kamloops Pulp and Paper Ltd. revealed that black liquor spills were responsible for substandard detoxification on some occasions. Effluents resulting from pulping green Douglas fir or spruce chips were sometimes associated with substandard detoxification, but not always. Evidence was found that residual toxic materials, whatever their source, might be resistant to biological treatment.

SERVIZI, J.A., D.W. MARTENS, and R.W. GORDON

1978

ACUTE TOXICITY AT ANNACIS ISLAND PRIMARY SEWAGE TREATMENT PLANT

PROGRESS REPT. NO. 38, INTERNATIONAL PACIFIC SALMON FISH. COMM., NEW WESTMINSTER, B.C., CANADA: 12 P.

Continuous flow and static bioassays of dechlorinated primary sewage were conducted at Annacis Island sewage treatment plant using fingerling sockeye salmon (Oncorhynchus nerka). Geometric mean survival time (CMST) was determined using undiluted effluent, and survival during 96 hr exposure to a range of dilutions was measured. Acute toxicity was greater during continuous flow than during static bioassays. In addition, acute toxicity was greater during dry weather than during wet weather flow conditions. Mortalities were usually 100% during bioassays of 65% v/v dechlorinated sewage but no mortalities occurred at 10% v/v.

Results were compared with acute toxicities measured at three other primary sewage treatment plants in the Greater Vancouver Sewerage and Drainage District, plus primary plants in San Francisco and Seattle.

Summation of toxic units attributed to anionic surfactants, un-ionized ammonia, cyanide, nitrite and metals measured failed to account for all the acute toxicity measured.

SERVIZI, J.A., E.T. STONE, and R.W. GORDON

1966

TOXICITY AND TREATMENT OF KRAFT PULP BLEACH PLANT WASTE

PROG. REPT. NO. 13, INT. PACIFIC SALMON FISH. COMM., NEW WESTMINSTER, B.C., CANADA: 34 P.

Some lethal and sub-lethal effects of neutralized kraft pulp bleach waste (NBW) on sockeye and pink salmon in fresh water were investigated. Sockeye and pink salmon alevins suffered reduced growth at concentrations of NBW much lower than those found toxic to fingerling sockeye. Prolonged exposure to dilute NBW resulted in deaths of adult migrant sockeye, but differences between adults and fingerlings in resistance to NBW was not demonstrated conclusively. Viability of sperm and ova was not reduced in the case of adult sockeye which survived exposure to NBW. Experiments with biological treatment of the waste indicated that, although the initial toxic and chemical strength of NBW varied widely, a reduction of BOD by about 60% would render the waste almost non-toxic to fingerling sockeye. Possible mechanisms by which lethal and sub-lethal toxic effects occur are discussed and recommendations are made for further research.

SERVIZI, J.A., R.W. GORDON, and D.W. MARTENS

1968

TOXICITY OF TWO CHLORINATED CATECHOLS, POSSIBLE COMPONENTS OF KRAFT PULP MILL BLEACH WASTE

PROGRESS REPT. NO. 17, INTERNATIONAL PACIFIC SALMON FISH. COMM., NEW WESTMINSTER, B.C., CANADA: 43 P.

Young pink salmon were less tolerant of tetrachlorocatechol than were sockeye. Advanced sockeye alevins were more tolerant of tetrachlorocatechol than were freshly hatched alevins, fry or smolts. Sublethal concentrations of di- and tetrachlorocatechol caused an increase in respiration rate which, it is believed, indicated disruption of cellular processes by uncoupling oxidative phosphorylation. Tetrachlorocatechol was apparently oxidized by biological treatment with activated sludge and it was concluded that all chlorinated catechols and phenols, except pentachlorophenol, would be oxidized by this treatment, if present in bleach waste. Toxic strengths of chlorinated catechols and phenols were between those of the non-chlorinated molecules and a common insecticide. Application of the results was discussed in light of the possible synergistic effects resulting from a mixture of chlorinated organic compounds and other toxicants of industrial and domestic origin.

SHEFFY, T.B. and J.R. ST. AMANT

1980

TOXIC SUBSTANCES SURVEY OF LAKE MICHIGAN, SUPERIOR AND TRIBUTARY STREAMS: FIRST ANNUAL REPORT

WISCONSIN DEPT. NATURAL RESOURCES: 96 P.

In July, 1979, the Department of Natural Resources received a grant from the Wisconsin Coastal Management program to conduct a systematic and comprehensive survey of 16 toxic substances in Wisconsin's coastal zone. The first year of the ongoing project involved the collection and analysis of 283 fish samples from 63 locations in the coastal zone, including 23 nearshore, 3 offshore and 37 tributary stream sampling stations along Lakes Michigan and Superior. The major objectives of this survey, the sampling plan and the findings are discussed.

SHUMWAY, D.L.

1968

THE EFFECTS OF UNBLEACHED KRAFT MILL EFFLUENTS ON SALMON. II. FLAVOR OF JACK COHO SALMON

TECH. BULL. NO. 217, NCASI, NEW YORK, NY: 47-53

A preliminary study was conducted on the influence of exposure to untreated and biologically treated unbleached kraft mill effluent on the flavor of coho salmon flesh. Measurable cooked flavor impairment resulted from exposure to untreated effluents for 72 to 96 hours at volume concentrations above 1.5 percent. No flavor impairment was noted when fish were exposed to 2.9 volume percent, the highest concentration tested, of biologically treated effluent.

JAMES R. ST. AMANT, MARY E. PARISO, AND THOMAS B. SHEFFY

1984

POLYCHLORINATED BIPHENYLS IN SEVEN SPECIES OF LAKE MICHIGAN FISH, 1971-1981

IN TOXIC CONTAMINANTS IN THE GREAT LAKES. ED.: O. NIRAGU AND S. SIMMONS,

JOHN WILEY AND SONS, INC. NEW YORK

In a recent study by the Wisconsin Department of Natural Resources, seven species of fish from Lake Michigan and Green Bay were monitored for PCBs from 1971 to 1981. An overall decrease in PCB concentration was observed for all species except walleye. High levels of PCBs (maximum 22,40 ppm) identified at the beginning of the study decreased steadily to the present condition where all species monitored were below the U.S. Food and Drug Administration tolerance level of 5.00 ppm. These trends demonstrate the effectiveness of legislation which banned production, established strict controls on use and disposal, and ultimately reduced the input of PCBs to Lake Michigan.

STERN, A.M. and C.R. WALKER

1978

HAZARD ASSESSMENT OF TOXIC SUBSTANCES: ENVIRONMENTAL FATE TESTING OF ORGANIC CHEMICALS AND ECOLOGICAL EFFECTS TESTING

IN: J. CAIRNS, JR., K.L. DICKSON, AND A.W. MAKI (EDS.), ESTIMATING THE HAZARD OF CHEMICAL SUBSTANCES TO AQUATIC LIFE, ASTM SPECIAL TECH. PUBL. 657, ASTM, PHILADELPHIA, PA: 81-131

In order to evaluate the potential hazards associated with the commercial use of chemical substances, an assessment of their ultimate environmental fate must be made. Fate, in this sense, can be defined as the transport and disposition of a chemical after it is released into the environment from a point source (manufacturing plant) or a disposal site (landfill, waste treatement plant, etc.). Determination of chemical fate could have considerable impact on predicting the potential adverse environmental effects of chemical pollutants, since it would help identify: (a) the areas over which pollutants would be distributed; (b) the types of reactions they would be subjected to during transport and after deposition; (d) the sensitive biological targets that would be brought under their influence; and (e) the sequence of biological tests and conditions relative to the site of impact, concentration, period of exposure, and specificity of biological impact. Therefore, tests designed to allow assessments to be made of the environmental fate of chemical contaminants must address the generic areas of chemical mobility and persistence, and toxicological and ecological significance of the exposure of the organism, population, and community.

Several studies have reviewed and evaluated test methods for determining the environmental fate of chemical contaminants. While these reports cover current test methods, few attempts have been made to design test protocols or to prioritize test for individual chemicals. Unfortunately, available documents on environmental fate testing indicate that the design of experimental procedures is often made on an ad hoc basis and is extremely variable. In contrast to the documentation of toxicity testing, literature concerned with environmental fate testing is virtually unknown. This lack of standardization is perhaps a result of the almost infinite ways that chemicals may be released into and reside in the environment. However, the hazard involved in using unstandardized tests is that, despite the expenditure of a great deal of money and effort, little insight is provided regarding the mobility of a chemical through the environment and its subsequent fate as a result of degradation and alteration processes. This is particularly true if the test is not well designed. Furthermore, the interpretation of unstandardized tests frequently varies and thus, in turn, makes it difficult to compare one chemical with another.

The following discussion is intended to furnish systematic guidelines for the testing of chemical-environmental fate. It is an attempt to provide a basis for constructing logical test protocols which are both cost effective and productive in that they would expedite reasonable adjudications concerning the safety of commercially useful chemicals. It must be emphasized that the development of any methodology is dependent upon the state of the art at the time it is devised. Therefore, the approach described here must be considered an interim solution to the problem of assessing the environmental fate of chemical pollutants and must be amenable to revision as new information and technologies are made available.

SULLIVAN, J.R. and J.J. DELFINO

1982

A SELECT INVENTORY OF CHEMICALS USED IN WISCONSIN'S LOWER FOX RIVER BASIN

UNIVERSITY OF WISCONSIN SEA GRANT INSTITUTE, MADISON, WI: 176 P

Increased awareness of the sources, distribution and fate of chemicals in natural waters led to an assessment of the use or production of these potentially hazardous materials in the Lower Fox River Basin in northeastern Wisconsin. The inventory is one phase of a program for assessing which organic compounds may be troublesome when they reach the aquatic environment. In effect, the inventory is a companion approach to an analytical effort designed to locate potentially toxic organic pollutants. Rather than doing countless and expensive scans on gas chromatography/mass spectrometry systems to identify organic compounds, certain chemicals can be traced down through an approach outside the laboratory. Though useful itself, the inventory must be interwoven with an analytical program so the findings may be applied to the aquatic environment.

In essence, the inventory provides a means of ascertaining the types of chemicals that may be expected to occur in the aquatic environment; then the analytical program can focus on or intensify its efforts by looking for specific compounds and their structurally altered products. When a chemical is identified from the inventory as being used, produced or manufactured within the basin, further effort can follow.

THOMANN, R.V.

1978

SIZE DEPENDENT MODEL OF HAZARDOUS SUBSTANCES IN AQUATIC FOOD CHAIN

ECOL. RES. SER., EPA-600/3-78-036, ENVIRON. RES. LAB., U.S. EPA, DULUTH, MN: 39 P.

In order to incorporate both bioaccumulation of toxic substances directly from the water and subsequent transfer up the food chain, a mass balance model is constructed that introduces organism size as an additional independent variable. The model represents an ecological continuum through size dependency; classical compartment analyses are therefore a special case of the continuous model. Size dependence is viewed as a very approximate ordering of trophic position.

The analysis of some PCB data in Lake Ontario is used as an illustration of the theory. A completely mixed water volume is used. Organism size is considered from 100 um to 10^6 um. PCB data were available for 64 um net hauls, alewife, smelt, sculpin and coho salmon. Laboratory data from the literature were used for preliminary estimates of the model coefficients together with the field data. The analysis indicated that about 30% of the observed 6.5 ug PCB/gm fish at the coho salmon size range is due to transfer from lower levels in the food chain and about 70% from direct water intake. The model shows rapid accumulation of PCB with organism size due principally to decreased excretion rates and decreased biomass at higher trophic levels.

The analysis indicates that if a level of 5 ug PCB/gm at 10^6 um is sought, total (dissolved and particulate) water concentration would have to be about 36 ng/l or about 66% of the present 55 ng/l.

U.S. ENVIRONMENTAL PROTECTION AGENCY, REGION V

1977

GUIDELINE FOR THE POLLUTIONAL CLASSIFICATION OF GREAT LAKES HARBOR SEDIMENTS

U.S. EPA, REGION V, CHICAGO, IL: 7 P.

Guidelines for the evaluation of Great Lakes harbor sediments, based on bulk sediment analysis, have been developed by Reigon V of the U.S. Environmental Protection Agency. These guidelines, developed under the pressure of the need to make immediate decisions regarding the disposal of dredged material, have not been adequately related to the impact of the sediments on the lakes and are considered interim guidelines until more scientifically sound guidelines are developed.

The guidelines are based on the following facts and assumptions:

1. Sediments that have been severely altered by the activities of men are most likely to have adverse environmental impacts.

2. The variability of the sampling and analytical techniques is such that the assessment of any sample must be based on all factors and not on any single parameter with the exception of mercury and polychlorinated biphenyls (PCBs).

3. Due to the documented bioaccumulation of mercury and PCBs, rigid limitations are used which override all other considerations.

Sediments are classified as heavily polluted, moderately polluted, or nonpolluted by evaluating each parameter measured against the scales shown below. The overall classification of the sample is based on the most predominant classification of the individual parameters. Additional factors such as elutriate test results, source of contamination, particle size distribution, benthic macroinvertebrate populations, color, and odor are also considered. These factors are interrelated in a complex manner and their interpretation is necessarily somewhat subjective.

VAN HORN, W.M., J.B. ANDERSON, and M. KATZ

1949

THE EFFECT OF KRAFT PULP MILL WASTES ON SOME AQUATIC ORGANISMS

TRANS. AM. FISH. SOC. 79:55-63

A study has been made of the toxic substances which may be found in kraft pulp-mill waste-waters. It has been determined that the sulphides, mercaptans, resin acid soaps, and sodium hydroxide constitute the greatest hazard. The minimum lethal concentration of these and other materials to fresh-water minnows, Daphnia, and aquatic insect larvae has been established. Methods have been devised for evaluating these materials in kraft-waste waters, and data from the examination of the wastes of a typical northern kraft mill are presented.

VEITH, G.D.

1975

BASELINE CONCENTRATIONS OF POLYCHLORINATED BIPHENYLS AND DDT IN LAKE MICHIGAN FISH, 1971

PESTIC. MONIT. J. 9(1):21-29

Responding to the recommendations of the Lake Michigan Interstate Pesticide Committee, the author aimed to establish baseline data on polychlorinated biphenys (PCBs) and DDT in Lake Michigan fish in 1971. Because the past 2 years had witnessed unprecedented legislative action to protect food resources and other aquatic species near the top of the food chain from persistent hazardous chemicals, the author also attempted to gauge the impact of cooperative legislative action on the quality of large lakes.

Thirteen species of fish taken from 14 regions of Lake Michigan in the fall of 1971 were analyzed for PCBs and DDT analogs. Mean wet-weight concentrations of PCBs similar to Aroclor 1254 ranged from 2.7 ppm in rainbow smelt to 15 ppm in lake trout. Most trout and salmon longer than 12 inches contained PCBs at concentrations greater than the tolerance level of 5 ppm established by the Food and Drug Administration, U.S. Department of Health, Education, and Welfare. Mean concentrations of total DDT ranged from less than 1 ppm in suckers to approximately 16 ppm in large lake trout. The presence of the major chlorinated hydrocarbons was confirmed by gas-liquid chromatography/mass spectrometry; additional PCB confirmations were obtained through perchlorination. The most abundant PCBs were tetra-, penta-, hexa-, and heptachlorobiphenyls which are similar to commercially prepared Aroclor 1254; lesser chlorinated PCBs were present in fish from nearshore waters.

WALDEN, C.C., T.E. HOWARD, and G.C. FROUD

1970

A QUANTITATIVE ASSAY OF THE MINIMUM CONCENTRATIONS OF KRAFT MILL EFFLUENTS WHICH AFFECT FISH RESPIRATION

WATER RES. 4:61-68

Procedural variables, in the buccal cavity technique for measuring the cough response of fish to kraft mill effluents, have been examined. The quantitative procedure which was developed can measure the threshold concentration level at which effluents produce respiration abnormalities in fish. The elapsed time requirement for this assay is the same as for an acute bioassay.

Minimum response concentrations, for neutralized pulping and bleaching effluents from a typical modern kraft pulp mill, were 1.1 and 4.0 per cent respectively.

The nature of aberrations observed in the respiration of fish exposed separately to pulping and bleaching effluents was identical, indicating that these effluents may contain similar toxic principles. Cough response observations indicate that fish acclimate to sublethal concentrations of kraft effluents, the time required for acclimation being related directly to the effluent concentration.

WARREN, C.E.

1972

PHASES I AND II: EFFECTS OF PULP AND PAPER MILL EFFLUENTS ON GROWTH AND PRODUCTION OF FISH

RES. GRANTS #B-004-ORE AND B-013-ORE, OFFICE WATER RESOURC. RES., U.S. DEPT. INTERIOR: 115 P

This report ia an Oregon State University research project on the effects of primary treated and of biologically stabilized kraft mill effluents on the growth and production of salmon and trout. The research was planned to be conducted in two phases.

Phase I was concerned with two kinds of laboratory studies of the effects of kraft mill effluents on salmon. In some of these laboratory studies, juvenile chinook salmon (Oncorhynchus tshawytscha) were held in continuous-flow aquaria or in exercise channels at different concentrations of kraft mill effluent and fed different ration levels, in order to determine the concentrations that have little or no direct effect on the relationship between the food consumption and growth rates of the fish.

Phase II of this research has been conducted in three large experimental stream channels, much more nearly representative of natural streams. Each stream channel is about 6 feet wide and 320 feet long, and each receives a flow of 0.67 cfs of water pumped from the Willamette River. Different species of salmon and trout were stocked in these stream channels, one of which received primary treated effluent for about one year, then biologically stabilized effluent for more than one year. Studies of the growth and production of the salmonids, their food habits, the kinds and availability of insects and other fish food organism, and the composition and density of the algal community component were conducted.

WARREN, C.E., J.H. WALES, G.E. DAVIS, and P. DOUDOROFF

1964

TROUT PRODUCTION IN AN EXPERIMENTAL STREAM ENRICHED WITH SUCROSE

J. Wildl. Manage. 28(4):617-660

From 1960 through 1963, three experiments were performed on the production, food habits, and food consumption of coastal cutthroat trout (Salmo clarki clarki) in sucrose-enriched and in unenriched sections of Berry Creek, a small woodland stream in the Willamette River Basin of Oregon. These experiments were part of a general investigation of the trophic pathways through which energy from light, organic debris, and dissolved organic matter enters into the production of fish and other organisms.

The flow in a 1,500-foot portion of Berry Creek was controlled by means of a diversion dam and a bypass canal. Four sections of this portion of the stream, each consisting of a riffle and a pool, were separated by fine screens which prevented the drifting of fish-food organisms from one section to the next. The water in two sections was continuously enriched by introducing a few milligrams of sucrose per liter, and most of the deciduous forest canopy was removed from one of the enriched and one of the unenriched sections. Only the enrichment with sucrose led to large and consistent increases in food consumption and production of trout: food consumption was increased about twofold and trout production usually much more than sevenfold. Trout production increased so much more than food consumption because only a relatively small portion of the comparatively large amount of food consumed in the enriched sections was required for maintenance of the trout stocks. The maintenance food produced and available in the unenriched sections was required for maintenance, with little left for promoting growth.

Food consumption values are believed to be more reliable measures of the relative productivity of the different sections for trout than are production values. Results of studies of food habits of the trout and available data on biomasses of insects in the riffles indicate that increased food consumption and production of trout in the enriched sections were made possible by greater abundance of aquatic food organisms, especially of tendipedid (chironomid) larvae, the consumption of terrestrial food being roughly equal in all sections. Introduction of sucrose resulted in growth of the bacterium Sphaerotilus natans, a slime organism frequently associated with organic pollution. This bacterial growth provided food and habitat for tendipedid larvae, the most important food organisms of trout in the enriched sections. Concepts of trophic relations in aquatic ecosystems and the application of these concepts to problems of water resource management are discussed in the light of the findings.

WARREN, C.E., W.K. SEIM, R.O. BLOSSER, A.L. CARON, and E.L. OWENS

1974

EFFECT OF KRAFT EFFLUENT ON THE GROWTH AND PRODUCTION OF SALMONID FISH

TAPPI 57(2): 127-132

Studies of the effects of kraft mill effluents - receiving only primary treatment or biological stabilization as well - on the growth of salmonid fish in aquaria and on their growth and production and the availability of their food organisms in laboratory stream communities and in large experimental stream channels were conducted over a period of 6 years. Neither primary treated nor secondary treated effluent had much, if any, effect on the growth of salmonids in aquaria at BOD concentrations below about 0.5 mg/liter, but these effluents usually did affect growth at higher concentrations. The effluents did not deleteriously affect the growth and production of salmonids in laboratory stream communities and experimental stream channels but did change the composition of the benthic community of algae and insects at a BOD concentration of 0.75 mg/liter.

WEBB, P.W. and J.R. BRETT

1972

THE EFFECTS OF SUBLETHAL CONCENTRATIONS OF WHOLE BLEACHED KRAFTMILL EFFLUENT ON THE GROWTH AND FOOD CONVERSION EFFICIENCY OF UNDERYEARLING SOCKEYE ...

J. FISH. RES. BOARD CAN. 29(11):1555-1569

Changes in growth rate and gross conversion efficiency were measured for underyearling sockeye salmon during and after exposure to full bleached kraft mill effluent (BKME). Five groups of fish were exposed for 56 days to 0, 1.0, 2.5, 10, and 25% BKME (v/v). Fresh 24-hr composite effluent at pH 6.8 was used daily after filtering. Growth was followed for a further 56 days after BKME exposure. Temperature was held at 15 C and dissolved oxygen between 90 and 100% air saturation. Growth rate and conversion efficiency were unaffected at 1.0 and 2.5% BKME. Reduced mean growth rate and conversion efficiency at 10% BKME were not statistically significant from controls but were considered to be biologically important in estimating threshold response levels. Significant reductions were found at 25% BKME. No recovery in retarded growth was found after exposure to BKME. Condition factor and percentage dry weight were not affected. It was concluded from computed response curves that the EC50 of the effluent was approximately 3.7% (v/v).

WECKWERTH, H.W. and B.A. FENSKE

1982

AUTOMATIC WATER QUALITY MONITORING OF THE FOX AND WISCONSIN RIVERS 1972-1981

WATER QUALITY EVALUATION SEC., BUREAU WATER RESOUR. MANAG., WISCONSIN DEPT. NAT. RESOUR., MADISON, WI: 325 P.

The automatic water quality monitoring system for the Lower Fox River and the Wisconsin River was installed in 1970-1971. The system consists of eleven stations, five on the Fox River and six on the Wisconsin River. All stations are located in existing buildings, either hydroelectric plants or papermills. No special heating arrangements were necessary except in some cases power supplies are covered or ventilated depending upon the season.

Two basic systems of flow are utilized. One system uses the head of the water source to supply a continuous flow to the monitor. The monitor in this installation is located below the source water level. The other system uses a nonsubmersible pump to lift the water to the water monitor.

About half the stations have been relocated from the original installation. All have been modified and refined to improve reliability and serviceability. Special emphasis has been placed upon getting reliable water flow to the monitor water chamber and achieving a reliable effluent system. This has involved designing water filter and flushing systems to fit the station. In cases of excessive debris, a filter system to assure adequate influent sample, yet prevent debris from affecting the monitor apparatus, is necessary for reliable performance.

Each station of the system is cleaned, checked and calibrated on an average of ten days to two week intervals depending upon the season and flow conditions.

Necessary repairs and electronic servicing and testing is done as required in addition to the routine maintenance.

After about ten years of operation, the performance is at about an 80 to 90 percent satisfactory unit response level. This includes all problem factors that affect system operation. Some of these factors are powerline failures, storms, computer downtime, teletype lines, plumbing apparatus, electronics, flow problems, hydroelectric plants repair and human error.

WISCONSIN DEPARTMENT OF NATURAL RESOURCES

1978

INVESTIGATION OF CHLORINATED AND NONCHLORINATED COMPOUNDS IN THE LOWER FOX RIVER WATERSHED

EPA 905/3-78-004 U.S. EPA, CHIGAGO, IL : 229 P.

This study was developed because of the increasing concern over potentially toxic chlorinated and nonchlorinated organic compounds entering the environment. The Lower Fox River was studied because of the large number of industrial and municipal wastewater treatment systems discharging to this 64-kilometer stretch of river. Effluents, surface water, seston, snowmelt, sediment, fish, and clams were sampled.

A total of 105 compounds were identified by gas chromatography/mass spectrometry. An additional 20 compounds were characterized but not conclusively identified. Twenty identified compounds are on the U.S. EPA Consent Decree Priority Pollutant List. The study indicates that PCBs and some other chloro-organic compounds are associated with effluent suspended solids and that solids removal reduces effluent contaminant concentrations.

Effluent concentration ranges in ug/L for compounds quantified by GC/MS were: benzothiazole 10-30, hydroxybenzothiazole 10-30, methyl thiobenzothiazole 10-40, trichloroquaiacols 10-60, tetrachloroguaiacol 10-50, dichlorophenol 15-40, Trichlorophenol 5-100, Tetrachlorophenol 2-20, Pentachlorophenol 5-40, dehydroabietic acid 100-8500, and PCBs 0.4-68.0. It is possible, but not proven, that some compounds were formed by process or effluent chlorination.

Clams were found to rapidly bioaccumulate PCBs. After a 27-28 day exposure, PCB concentrations in clams ranged from 255 to 740 ug/kg. Fish fillet samples contained PCB concentrations up to 90 mg/kg. Sediments throughout most of the river were found to be contaminated with PCBs. Toxicity data are lacking on many of the identified compounds and additional data are needed.

WISCONSIN DEPARTMENT OF NATURAL RESOURCES

1978

FOX RIVER WASTE LOAD ALLOCATION-MODEL DATA

WATER QUALITY EVALUATION SECTION, DIV. OF ENVIRON. STANDARDS, WISCONSIN DEPT. NAT. RESOUR., MADISON, WI: 75 P.

Water Quality Surveys were conducted in the Lower Fox River and Green Bay between the DePere Dam and Long Tail Point. A slow long term improving trend can be seen in comparison to previous years, but the river and inner bay are still heavily enriched, causing heavy algae blooms. Dissolved oxygen and temperature stratification still occur occasionally. Sediment Oxygen Demand is lower than in previous years.

WI D.N.R., U.S.G.S., U.S. FISH WILDL. SERV., U.S. EPA REGION V, and UNIV. WI WATER CHEM. DEPT.

1983

FINAL REPORT OF THE TOXIC SUBSTANCES TASK FORCE ON THE LOWER FOX RIVER SYSTEM

WI DEPT. NAT. RESOUR., U.S. GEOL. SURV., U.S. FISH WILDL. SERV., U.S. EPA REGION V, and UNIV. WI WATER CHEM. DEPT.: 70 P.

More than 100 chemicals have been identified in the Lower Fox River System. The chemicals have been placed into categories based on their known or potential effects on man or fish and wildlife. Chemicals of primary concern (Category I) are those which may cause chronic toxicity to humans or other animals through consumption of fish and wildlife, and those which may cause acute/chronic toxicity or taste and odor effects to fish and wildlife of the Lower Fox River and Green Bay. Chemicals in category I include PCBs, PCDDs, PCDFs, resin and chlorinated resin acids, chlorophenols and ammonia. This category is the main focus of this report. Chemicals placed in Category II (found less frequently than Category I chemicals and not believed to be a problem) and Category III (present but effects uncertain) are not reviewed in detail.

PCBs

Polychlorinated biphenyls (PCBs) are documented as being present in the Fox River/Green Bay ecosystem. Although PCBs are considered toxic pollutants and a large toxicological data base exists, some uncertainties remain in the overall understanding of toxic effects. Of particular significance is the fact that microcontaminants in PCB mixtures, such as the polychlorinated-dibenzofurans, may be responsible for some of the observed toxic effects. The dominant PCB mixture identified in the Fox River, Aroclor 1242, comes from wastewater discharges associated with secondary fiber paper mills which deink carbonless copy paper.

PCDDs

Polychlorinated dibenzo-p-dioxins (PCDDs), particularly 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), are extremely toxic compounds. The degree of chloronation and substitution pattern on the parent dioxin molecule determines its toxicity. PCDDs occur as microcontaminants of chlorinated phenols, such as 2,4,5-trichlorophenol and pentachlorophenol.

PCDFs

Polychlorinated dibenzofurans (PCDFs) are not well-studied compounds. Certain isomers are extremely toxic to certain species, rivalling certain dioxin isomers in toxicity. The existence of PCDFs in the Fox River/Green Bay system is suspected because they occur as contaminants of PCB mixtures and various chlorinated phenolic compounds.

Resin and Chlorinated Resin Acids

Resin acids are naturally occurring compounds in the environment. They occur in wood, especially pine species, and are released to the aquatic environment through the pulping of wood. Resin acids are also a major component of rosin size, a raw material used by the pulp and paper industry.

Chlorophenols

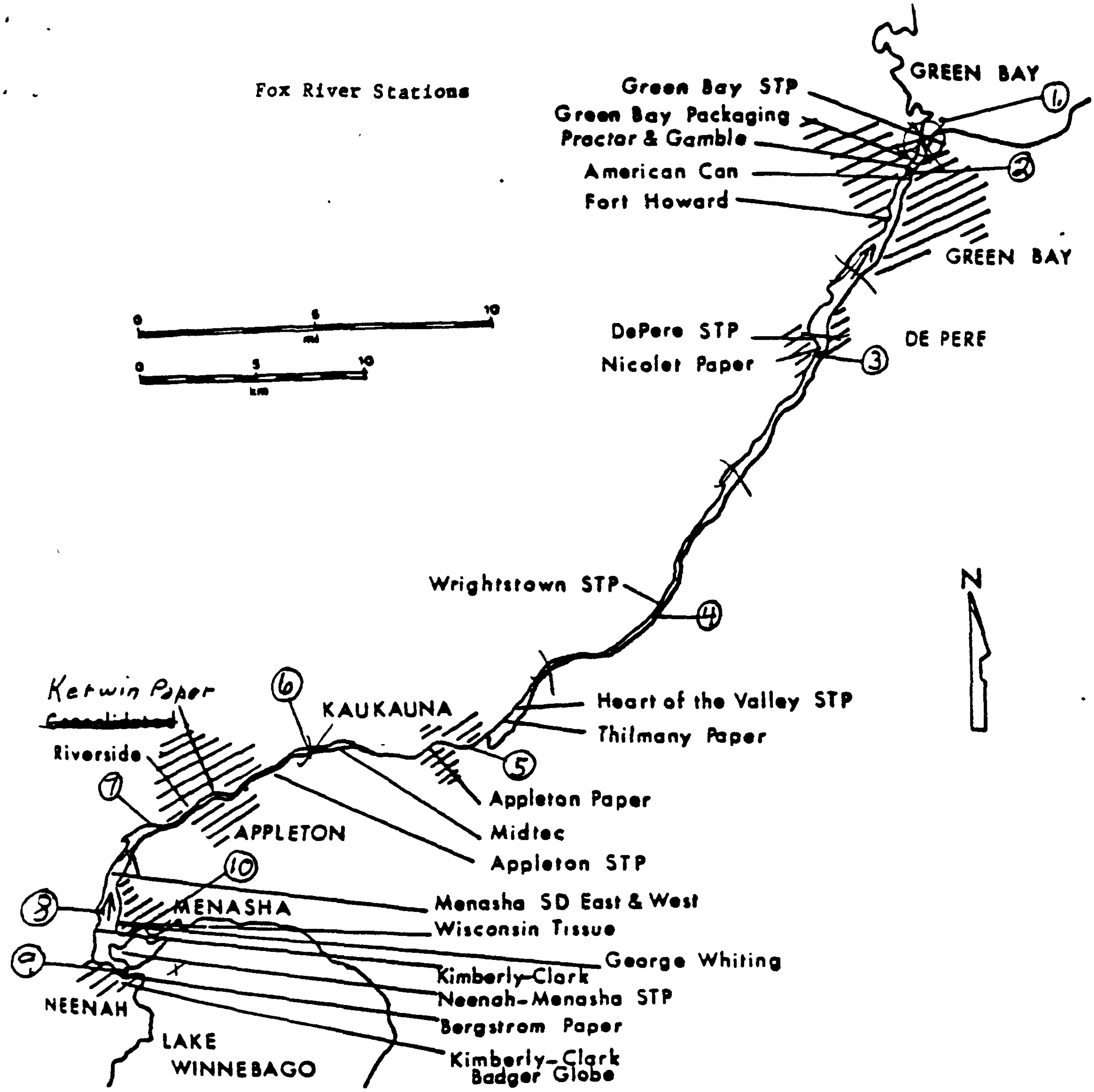
Most chlorophenols, especially pentachlorophenol, have an adequate toxicological data base. It should be noted, however, that the presence of chlorinated dioxins as micro contaminants in certain commercial chlorophenol mixtures accounts for a substantial portion of chlorophenol toxicity.

Ammonia

Ammonia is a naturally occurring compound found in all surface water as the decay product of nitrogen-containing organic matter. Ammonia is also found in sewage effluents and some industrial discharges.

APPENDIX B

Fox River Stations



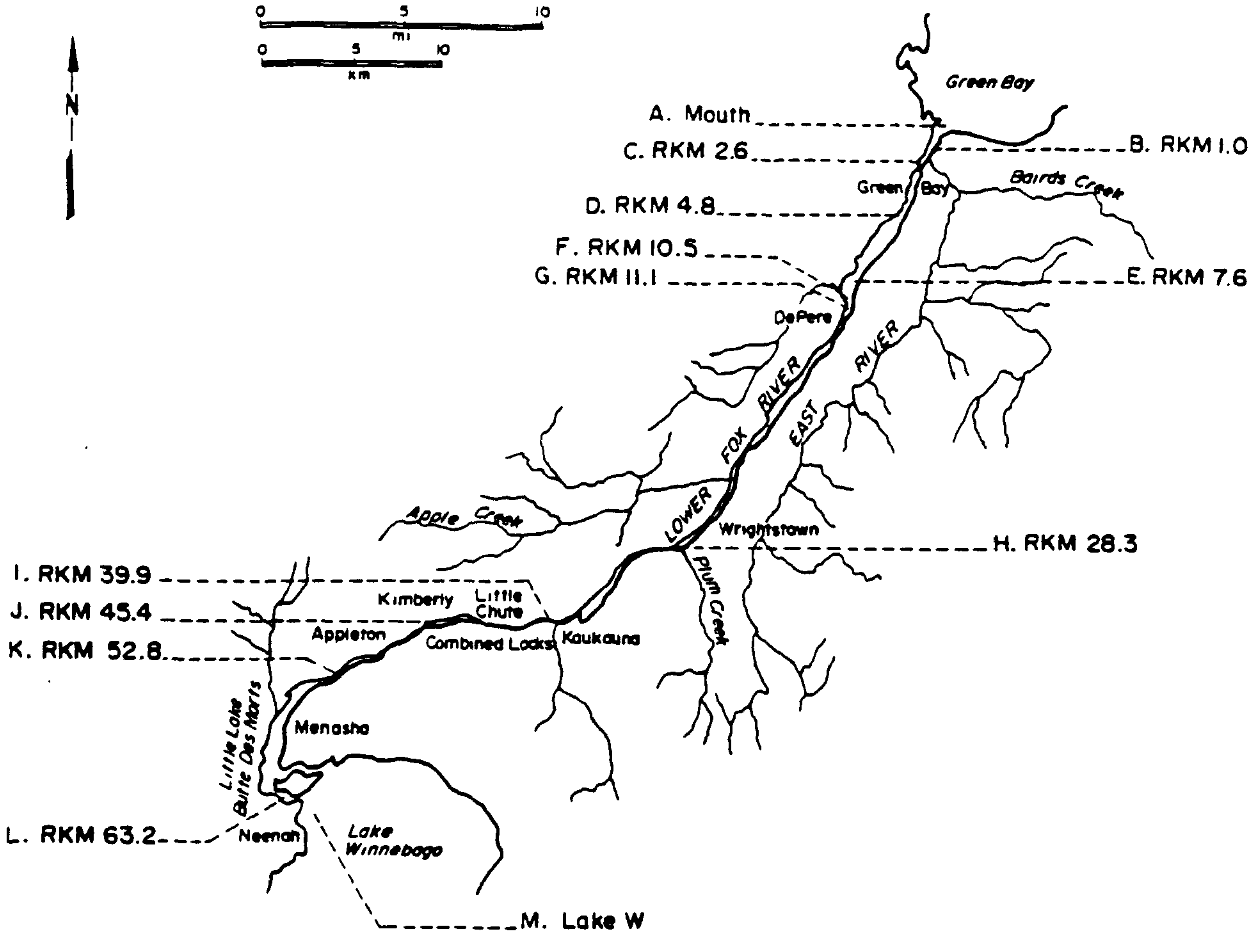
Municipal and Industrial Waste Discharges to the Lower Fox River.
(Anon, 1985)

Toxicity and Percent of Stream Flow of Effluent Discharges to the Fox River. (Anon, 1985)

Effluent ID or River Station No.	FHM NOEL % Concentration	Daphnid NOEL % Concentration	% Stream Flow at Sample Time	% Stream at 7Q10
Bergstrom Paper	70.7	70.7	.121	.624%
Kimberly Clark J	**	>100	.137	.704
Kimberly Clark L	>100	35.4	.052	.268
Kerwin Paper	**	**	.021	.202
Appleton Paper	**	70.7	.088	.842
Mid-Tech. Paper	**	**	.186	1.768
Wisconsin Tissue	**	**	.140	.411
Nicolet Paper	**	>100	.258	.757
Thilmany Paper	**	>100	.680	1.992
Green Bay STP	17.7	<100*	.92	5.35
Neenah-Menasha STP	>100	**	.22	1.20
Fort Howard Paper	70.7	**	.54	2.89
James River Paper	>100	**	.23	1.62
Kerwin Paper (2)	>100	<100*	.05	.31
Proctor Gamble	70.7	70.7	.11	.82
Green Bay Packaging	>100	>100	.22	1.53
Mid Tech (2)	>100	**	.26	1.52
Appleton STP	35.4	35.4	.28	1.51

* Not calculable at concentrations lower than 100% due to toxicity of dilution water.

** Not calculable



Map of Study Area and Locations of Sampling Stations for Toxicity Evaluation of Lower Fox River Water and Sediments (RKM = river kilometers). (Lien et al., 1985)

Physical and Chemical Data for Water Collected From the Lower Fox River at Various Locations and Dates

Sampling Station[1] (Lien et al., 1985)

Jan. 30-31, 1985	A	B	C	D	E	F	G	H	I	J	K	L	M
pH	7.96	7.97	8.00	8.05	-	-	8.08	8.02	-	-	7.99	-	8.19
alkal mg/l	164.8	163.8	163.4	163.6	-	-	168.9	162.9	-	-	166.6	-	172.4
cond μs/cm	397	361	309	318	-	-	360	362	-	-	328	-	367
hardness mg/l	193.9	188.0	187.6	189.4	-	-	195.1	188.4	-	-	188.4	-	197.4
Cl mg/l	18	10	14	14	-	-	13	13	-	-	13	-	11
NO_2 mg/l	<0.2	<0.2	<0.2	<0.2	-	-	<0.2	<0.2	-	-	<0.2	-	<0.2
NO_3 mg/l	0.9	1.4	1.4	1.4	-	-	1.5	1.4	-	-	1.3	-	1.3
PO_4 mg/l	<0.2	<0.2	<0.2	<0.2	-	-	<0.2	<0.2	-	-	<0.2	-	<0.2
SO_4 mg/l	22.7	19.7	19.7	20.2	-	-	19.7	18.3	-	-	14.8	-	16.8
NH_4^+ mg/l (total)	0.56	0.24	0.26	0.23	-	-	0.23	0.16	-	-	0.05	-	0.34
NH_3-N mg/l[2]	0.015	0.007	0.008	0.008	-	-	0.008	0.005	-	-	0.002	-	0.015
sulfides mg/l	<1.0	<1.0	<1.0	<1.0	-	-	<1.0	<1.0	-	-	<1.0	-	<1.0
March 13-14, 1985													
temp °C[3]	3	3	3	3	-	-	3	-	3	3	3	-	-
pH	7.63	7.80	7.87	7.78	-	-	7.94	7.94	7.94	7.83	7.75	7.67	7.61
alkal mg/l	133.6	146.4	145.7	132.7	-	-	158.5	160.9	165.8	166.3	164.0	168.2	155.3
cond μs/cm	440	380	348	379	-	-	355	412	383	399	415	395	378
hardness mg/l	164.9	175.5	178.0	166.5	-	-	180.4	189.6	198.9	194.9	194.9	192.9	187.4
Cl mg/l	20	16	16	20	-	-	14	13	13	13	17	10	10
NO_2 mg/l	<0.05	<0.05	<0.05	<0.05	-	-	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
NO_3 mg/l	4.0	4.0	4.0	4.4	-	-	3.8	3.5	3.4	4.0	3.7	3.0	0.8
PO_4 mg/l	<0.15	<0.15	<0.15	<0.15	-	-	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
SO_4 mg/l	22.5	19.0	19.0	19.5	-	-	18.5	18.5	17.7	17.0	19.2	14.5	13.5
NH_4^+ mg/l (total)	1.07	0.40	0.44	0.64	-	-	0.24	0.18	0.13	0.16	0.28	0.10	0.05
NH_3-N mg/l[2]	0.014	0.008	0.010	0.012	-	-	0.006	0.005	0.003	0.003	0.005	0.002	0.001
sulfides mg/l	<1.0	<1.0	<1.0	<1.0	-	-	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
April 30, 1985													
temp °C[3]	18	17	17	17	18	19	19	-	18	18	18	17	-
pH	8.38	8.90	8.75	8.65	8.95	8.93	8.98	-	9.01	9.3	9.06	9.27	-
alkal mg/l	153.7	141.8	141.3	144.8	138.3	140.4	140.4	-	140.8	140.4	148.4	139.0	-
cond μs/cm	419	300	315	315	273	310	285	-	300	282	290	275	-
hardness mg/l	188.1	159.1	159.2	162.7	158.7	159.6	160.2	-	158.4	159.6	162.3	164.2	-
Cl mg/l	31.3	13.4	13.6	16.4	11.4	11.4	11.6	-	11.4	11.4	13.1	9.5	-
NO_2 mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	-	<0.05	<0.05	<0.05	<0.05	-
NO_3 mg/l	1.1	1.1	1.1	1.2	1.0	0.4	0.9	-	0.8	0.8	0.6	0.4	-
PO_4 mg/l	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	-	<0.10	<0.10	<0.10	<0.10	-
SO_4 mg/l	36.0	16.0	16.0	18.0	15.0	16.0	15.0	-	15.0	15.0	16.0	13.0	-
NH_4^+ mg/l (total)	1.93	0.26	0.24	0.33	0.28	0.40	0.26	-	0.30	0.33	0.28	0.16	-
NH_3-N mg/l[2]	0.102	0.048	0.035	0.039	0.057	0.078	0.055	-	0.066	0.115	0.069	0.051	-
sulfides mg/l	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	-	<1.0	<1.0	<1.0	<1.0	-

[1] See Figure 1

[2] Unionized ammonia calculated from total ammonia as NH_4^+ using the table in Appendix A-1 from Thurston et al. 1979[16].

[3] At time of collection

Decoded percentage survival (i.e. grand average) of young walleye of different developmental phases for three stock sources from Wisconsin waters. (Hokanson and Lien, 1986)

Phase of development	Lower Fox River	Sturgeon Bay	Chippewa Flowage	P [a]
	Source			
Prolarvae (P_1)	[b] 96.3	98.4	98.1	0.7168
Postlarvae I (P_2)	73.3	58.9	90.8	0.0001
Postlarvae II (P_3)	84.3	94.8	95.2	0.0830
Juvenile (P_4)	96.4	97.0	90.6	0.2683
Overall survival [c]	53.8	51.6	72.3	0.0440

[a] Probability level of significance in survival of young walleyes among sources as determined by ANOVA.

[b] Underscore signifies no significant differences in mean response for the indicated stock source ($p < .05$; Tukey's multiple range test).

[c] Overall survival probability for a given stock is equal to $P_1 \times P_2 \times P_3 \times P_4$ where Pi is expressed as a decimal fraction for survival of offspring from each female.

Water chemistry at river intake during hatching experiments
(Auer and Auer, 1986)

Date	pH	DO (mgO_2/L)	NH_3-N (ugN/L)	NO_2-N (ugN/L)	H_2S (ug/L)
4/18	8.76	14.6	110	8	0.9
4/19	8.94	16.5	80	9	0.8
4/20	8.70	11.0	86	9	0.9
4/21	8.97	12.8	129	9	0.5
4/22	8.83	10.3	187	7	0.8
4/23	8.88	9.5	162	4	0.7
4/24	8.82	10.0	153	5	0.8
4/25	8.88	11.0	183	11	0.6
4/26	8.87	10.4	44	11	0.6
4/27	8.54	10.5	159	7	1.6
4/28	8.91	11.0	203	12	0.7
4/29	8.90	10.6	207	10	0.7
4/30	8.92	10.6	205	10	0.6
5/1	8.94	10.2	74	9	0.5
Mean	8.85	11.4	142	9	0.8

Chemical conditions at the sediment-water interface
(Auer and Auer, 1986)

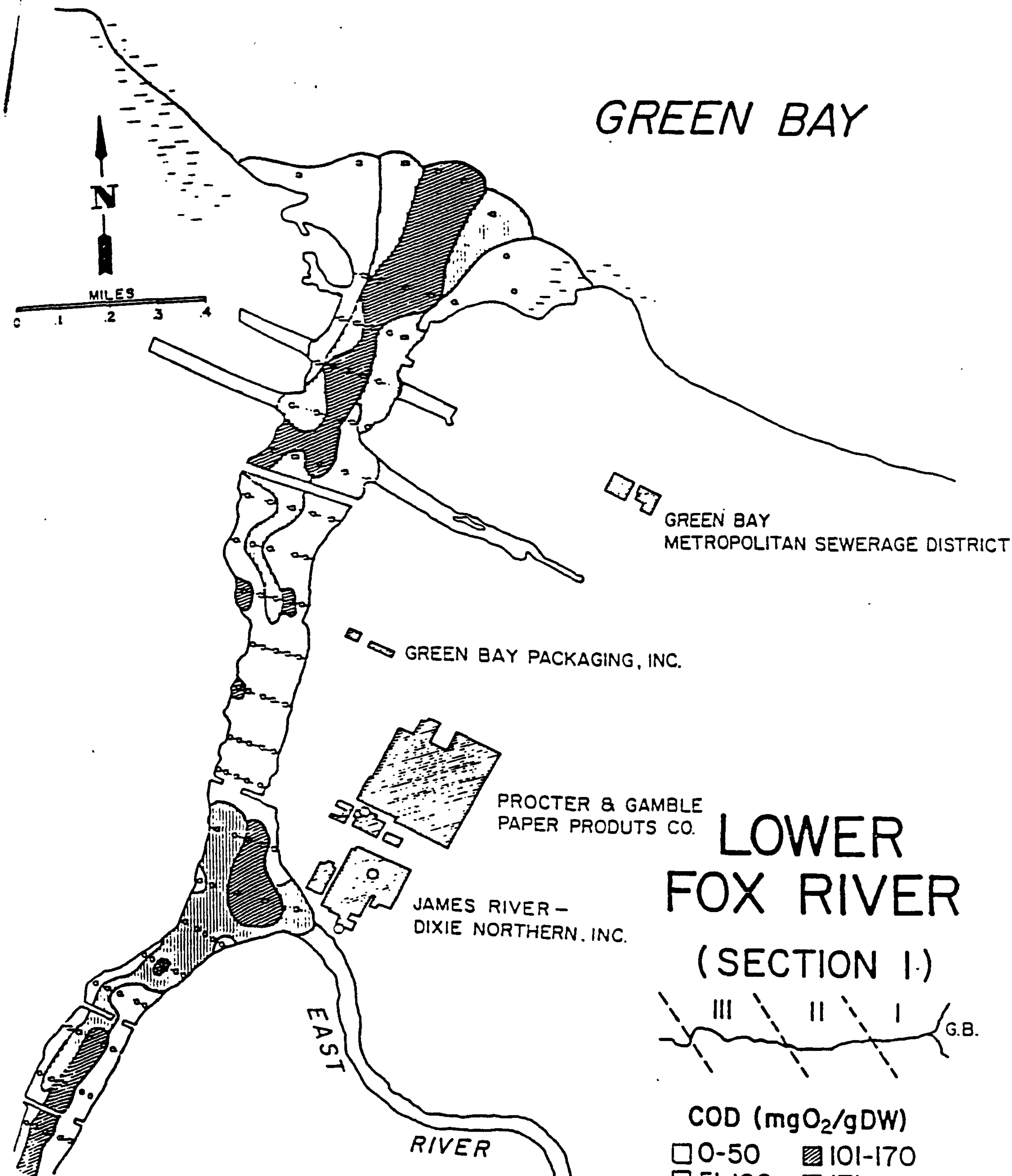
24 June 1985 - Temperature = 22 °C

Station	pH	DO (mgO_2/L)	NH_3-N (ugN/L)	NO_2-N (ugN/L)	Sed. COD (mgO_2/gDW)	H_2S (ug/L)
1	7.45	6.6	105	48	12	9.7
2	7.22	5.9	289	64	41	16.6
3	8.23	5.3	143	54	16	3.3
4	8.11	6.4	99	55	24	3.6
5	7.65	0.2	817	68	183	43.8
6	7.39	0.5	1874	15	157	55.5
7	7.54	4.0	163	21	353	89.2
8	7.75	3.1	386	37	463	11.5
9	8.25	6.9	168	61	27	1.8
10	8.18	4.2	257	46	319	4.8

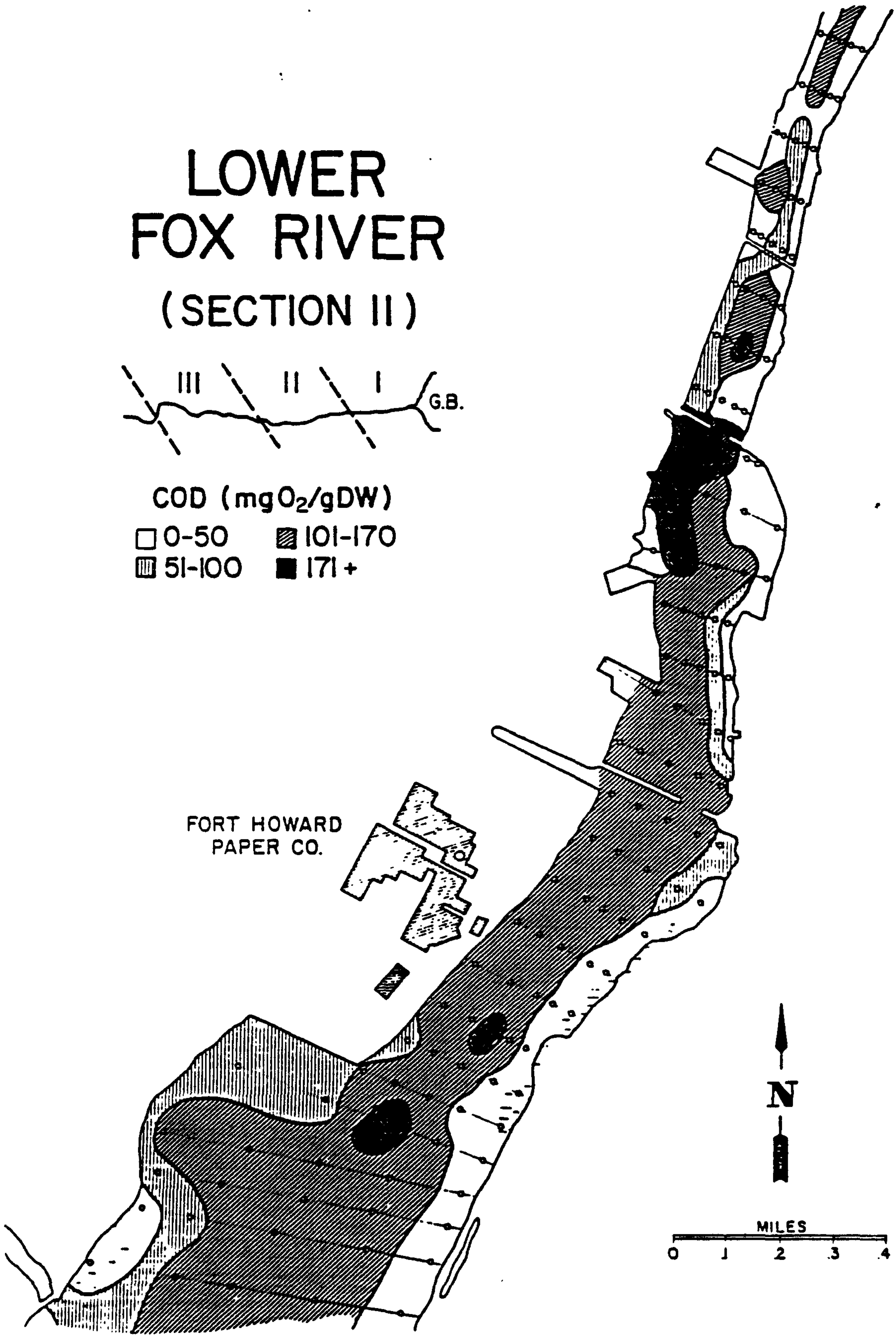
14 August 1985 - Temperature = 24 °C

Station	pH	DO (mgO_2/L)	NH_3-N (ugN/L)	NO_2-N (ugN/L)	Sed. COD (mgO_2/gDW)	H_2S (ug/L)
1	7.31	3.9	115	--	26	17.5
2	7.59	5.3	155	--	13	7.7
3	7.86	6.9	84	--	6	5.1
4	7.73	6.8	272	--	39	8.2
5	7.47	0.6	2339	--	224	189.9
6	7.49	0.9	2372	--	140	95.0
7	7.32	2.9	1778	--	375	289.9
8	7.36	1.5	5199	--	224	237.0
9	8.43	7.2	74	--	--	1.7
10	8.45	7.0	73	--	--	1.7

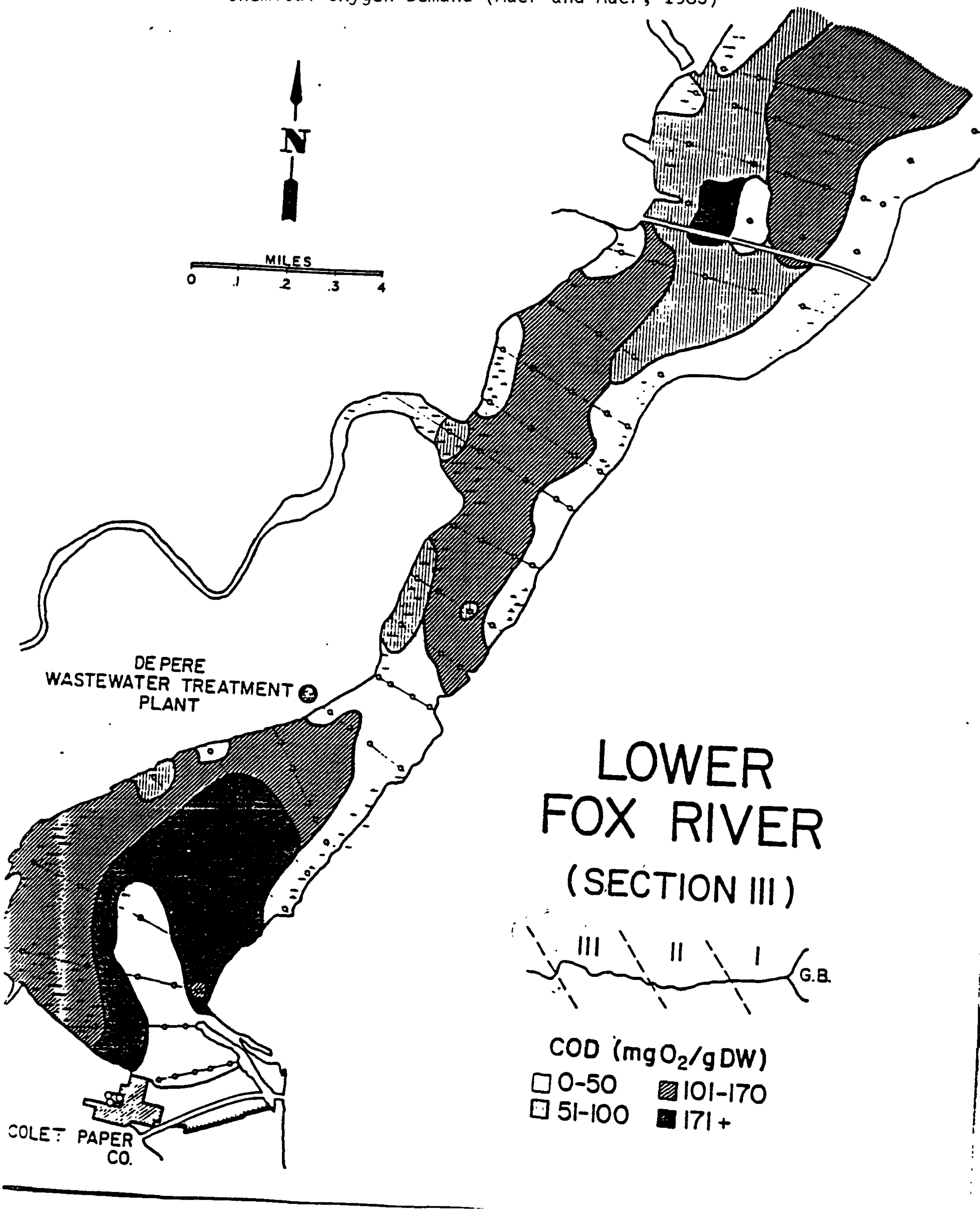
Chemical Oxygen Demand (Auer and Auer, 1983)



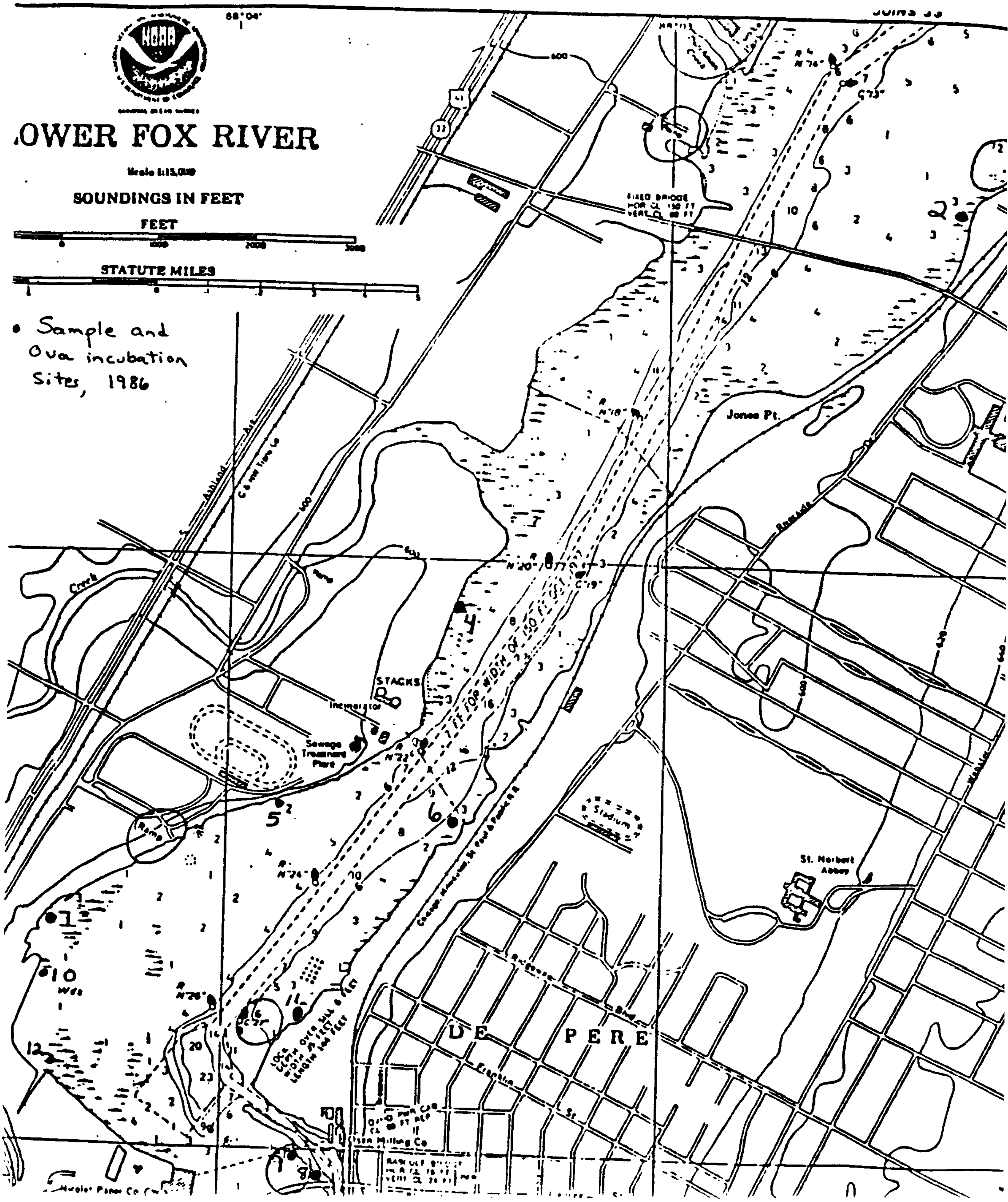
Chemical Oxygen Demand (Auer and Auer, 1983)



Chemical Oxygen Demand (Auer and Auer, 1983)



Walleye Egg Incubation Sites in 1986 (Brooke et al., 1986)



Survival of walleye ova incubated in non-groomed tissue culture triads during April 1986. (Average of all replicates and all females, uncorrected for initial ova viability). (Brooke et al., 1986)

Site Number	Percent Survival to Hatch
9	38.2
2	36.9
8	34.7
11	27.7
5	9.5
4	8.7
6	1.9
7	0.9
10	0

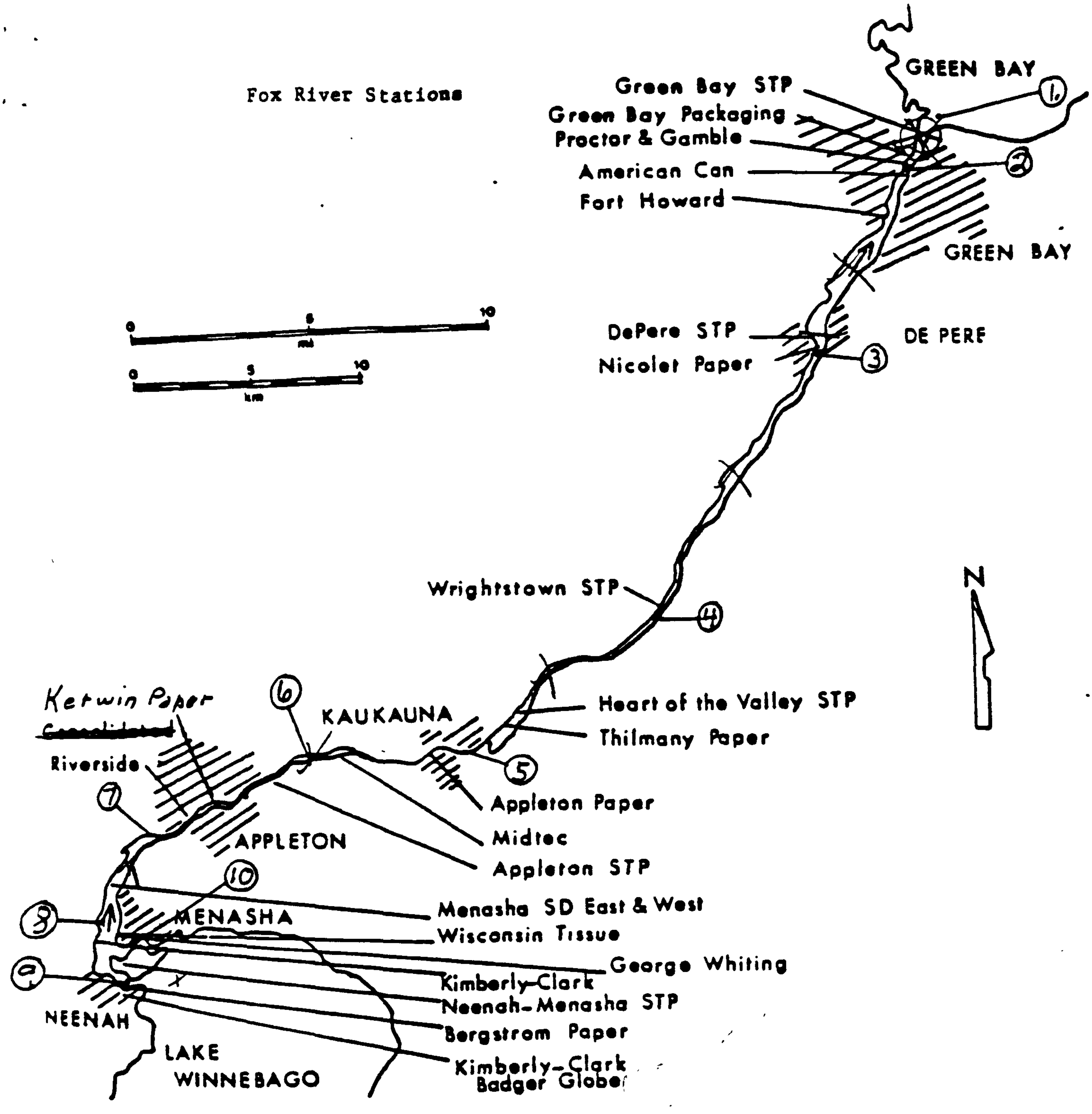
Abundance of Fish Species Caught by Fyke Nets in the Lower Fox River, April, 1985 (Balcer et al. 1986)

Walleye (Stizostedion vitreum vitreum)	792*
Yellow Perch (Perca flavescens)	807
Carp (Cyprinus carpio)	122
White Bass (Morone chrysops)	113
White Sucker (Catostomus commersoni)	106
Black Bullhead (Ictalurus melas)	22
Quillback (Carpoides cyprinus)	18
Northern Pike (Esox lucius)	11
Brown Bullhead (Ictalurus nebulosus)	8
Freshwater Drum (Aplodinotus grunniens)	7
Sauger (Stizostedion canadense)	4
Channel Catfish (Ictalurus punctatus)	4
Rock Bass (Ambloplites rupestris)	3
Burbot (Lota lota)	3
Crappie (Pomoxis sp.)	2
Redhorse Sucker (Moxostoma sp.)	1
Longnose Sucker (Catostomus catostomus)	1
Trout Perch (Percopsis omiscomaycus)	1

* Walleye collected from 22 net lifts; other species enumerated in 8 lifts.

APPENDIX B

Fox River Stations



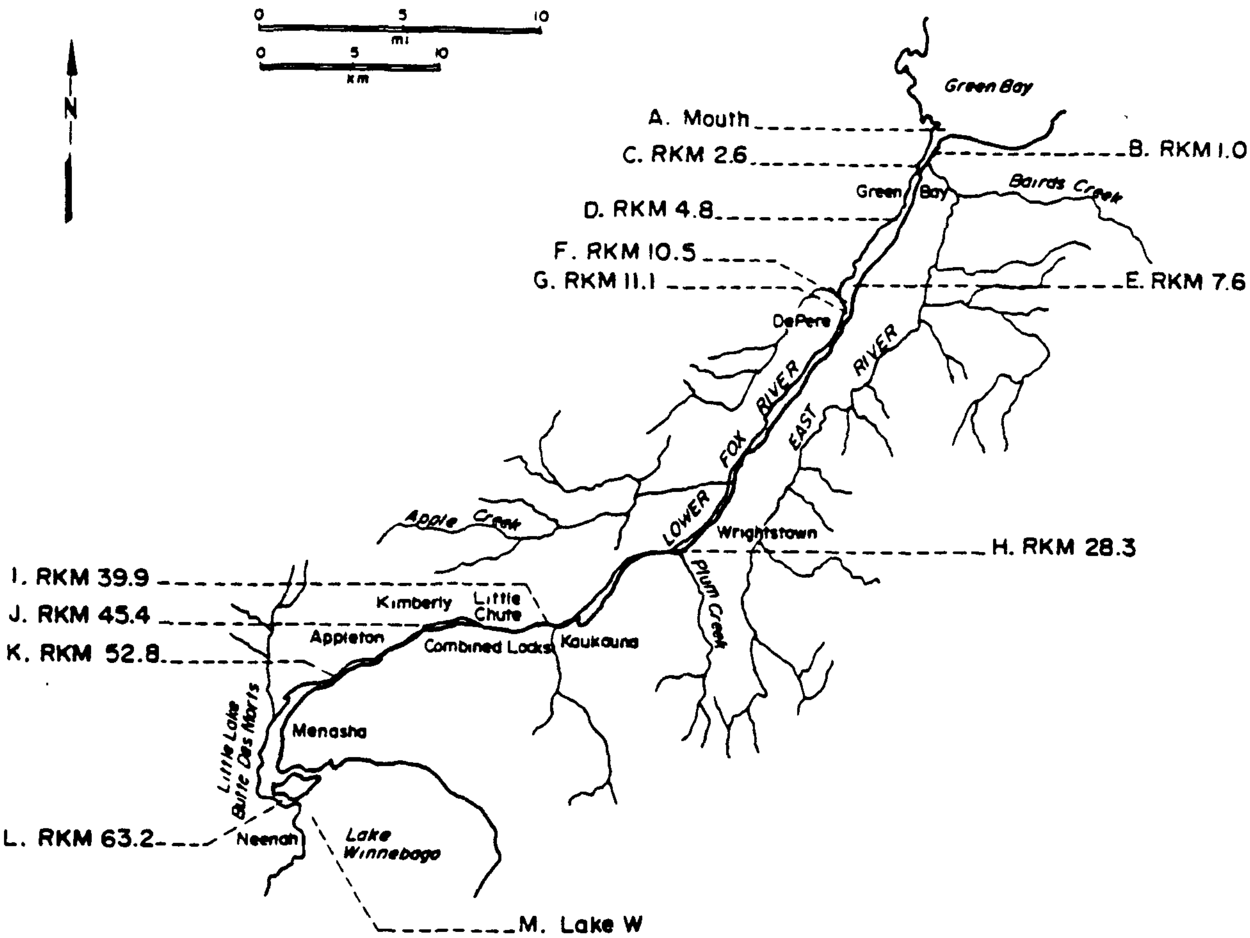
Municipal and Industrial Waste Discharges to the Lower Fox River.
(Anon, 1985)

Toxicity and Percent of Stream Flow of Effluent Discharges to the Fox River. (Anon, 1985)

Effluent ID or River Station No.	FHM NOEL % Concentration	Daphnid NOEL % Concentration	% Stream Flow at Sample Time	% Stream at 7Q10
Bergstrom Paper	70.7	70.7	.121	.624%
Kimberly Clark J	**	>100	.137	.704
Kimberly Clark L	>100	35.4	.052	.268
Kerwin Paper	**	**	.021	.202
Appleton Paper	**	70.7	.088	.842
Mid-Tech. Paper	**	**	.186	1.768
Wisconsin Tissue	**	**	.140	.411
Nicolet Paper	**	>100	.258	.757
Thilmany Paper	**	>100	.680	1.992
Green Bay STP	17.7	<100*	.92	5.35
Neenah-Menasha STP	>100	**	.22	1.20
Fort Howard Paper	70.7	**	.54	2.89
James River Paper	>100	**	.23	1.62
Kerwin Paper (2)	>100	<100*	.05	.31
Proctor Gamble	70.7	70.7	.11	.82
Green Bay Packaging	>100	>100	.22	1.53
Mid Tech (2)	>100	**	.26	1.52
Appleton STP	35.4	35.4	.28	1.51

* Not calculable at concentrations lower than 100% due to toxicity of dilution water.

** Not calculable



Map of Study Area and Locations of Sampling Stations for Toxicity Evaluation of Lower Fox River Water and Sediments (RKM = river kilometers). (Lien et al., 1985)

Physical and Chemical Data for Water Collected From the Lower Fox River at Various Locations and Dates (Lien et al., 1985)

Sampling Station[1]

	A	B	C	D	E	F	G	H	I	J	K	L	M
Jan. 30-31, 1985													
pH	7.96	7.97	8.00	8.05	-	-	8.08	8.02	-	-	7.99	-	8.19
alkal mg/l	164.8	163.8	163.4	163.6	-	-	168.9	162.9	-	-	166.6	-	172.4
cond µs/cm	397	361	309	318	-	-	360	362	-	-	328	-	367
hardness mg/l	193.9	188.0	187.6	189.4	-	-	195.1	188.4	-	-	188.4	-	197.4
Cl mg/l	18	10	14	14	-	-	13	13	-	-	13	-	11
NO_2 mg/l	<0.2	<0.2	<0.2	<0.2	-	-	<0.2	<0.2	-	-	<0.2	-	<0.2
NO_3 mg/l	0.9	1.4	1.4	1.4	-	-	1.5	1.4	-	-	1.3	-	1.3
PO_4 mg/l	<0.2	<0.2	<0.2	<0.2	-	-	<0.2	<0.2	-	-	<0.2	-	<0.2
SO_4 mg/l	22.7	19.7	19.7	20.2	-	-	19.7	18.3	-	-	14.8	-	16.8
NH_4^+ mg/l (total)	0.56	0.24	0.26	0.23	-	-	0.23	0.16	-	-	0.05	-	0.34
NH_3-N mg/l[2]	0.015	0.007	0.008	0.008	-	-	0.008	0.005	-	-	0.002	-	0.015
sulfides mg/l	<1.0	<1.0	<1.0	<1.0	-	-	<1.0	<1.0	-	-	<1.0	-	<1.0
March 13-14, 1985													
temp °C[3]	3	3	3	3	-	-	3	-	3	3	3	-	-
pH	7.63	7.80	7.87	7.78	-	-	7.94	7.94	7.94	7.83	7.75	7.67	7.61
alkal mg/l	133.6	146.4	145.7	132.7	-	-	158.5	160.9	165.8	166.3	164.0	168.2	155.3
cond µs/cm	440	380	348	379	-	-	355	412	383	399	415	395	378
hardness mg/l	164.9	175.5	178.0	166.5	-	-	180.4	189.6	198.9	194.9	194.9	192.9	187.4
Cl mg/l	20	16	16	20	-	-	14	13	13	13	17	10	10
NO_2 mg/l	<0.05	<0.05	<0.05	<0.05	-	-	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
NO_3 mg/l	4.0	4.0	4.0	4.4	-	-	3.8	3.5	3.4	4.0	3.7	3.0	0.8
PO_4 mg/l	<0.15	<0.15	<0.15	<0.15	-	-	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15	<0.15
SO_4 mg/l	22.5	19.0	19.0	19.5	-	-	18.5	18.5	17.7	17.0	19.2	14.5	13.5
NH_4^+ mg/l (total)	1.07	0.40	0.44	0.64	-	-	0.24	0.18	0.13	0.16	0.28	0.10	0.05
NH_3-N mg/l[2]	0.014	0.008	0.010	0.012	-	-	0.006	0.005	0.003	0.003	0.005	0.002	0.001
sulfides mg/l	<1.0	<1.0	<1.0	<1.0	-	-	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
April 30, 1985													
temp °C[3]	18	17	17	17	18	19	19	-	18	18	18	17	-
pH	8.38	8.90	8.75	8.65	8.95	8.93	8.98	-	9.01	9.3	9.06	9.27	-
alkal mg/l	153.7	141.8	141.3	144.8	138.3	140.4	140.4	-	140.8	140.4	148.4	139.0	-
cond µs/cm	419	300	315	315	273	310	285	-	300	282	290	275	-
hardness mg/l	188.1	159.1	159.2	162.7	158.7	159.6	160.2	-	158.4	159.6	162.3	164.2	-
Cl mg/l	31.3	13.4	13.6	16.4	11.4	11.4	11.6	-	11.4	11.4	13.1	9.5	-
NO_2 mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	-	<0.05	<0.05	<0.05	<0.05	-
NO_3 mg/l	1.1	1.1	1.1	1.2	1.0	0.4	0.9	-	0.8	0.8	0.6	0.4	-
PO_4 mg/l	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	-	<0.10	<0.10	<0.10	<0.10	-
SO_4 mg/l	36.0	16.0	16.0	18.0	15.0	16.0	15.0	-	15.0	15.0	16.0	13.0	-
NH_4^+ mg/l (total)	1.93	0.26	0.24	0.33	0.28	0.40	0.26	-	0.30	0.33	0.28	0.16	-
NH_3-N mg/l[2]	0.102	0.048	0.035	0.039	0.057	0.078	0.055	-	0.066	0.115	0.069	0.051	-
sulfides mg/l	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	-	<1.0	<1.0	<1.0	<1.0	-

[1] See Figure 1
[2] Unionized ammonia calculated from total ammonia as NH_4^+ using the table in Appendix A-1 from Thurston et al. 1979[16].
[3] At time of collection

Decoded percentage survival (i.e. grand average) of young walleye of different developmental phases for three stock sources from Wisconsin waters. (Hokanson and Lien, 1986)

	Source			
Phase of development	Lower Fox River	Sturgeon Bay	Chippewa Flowage	P [a]
Prolarvae (P_1)	[b] 96.3	98.4	98.1	0.7168
Postlarvae I (P_2)	73.3	58.9	90.8	0.0001
Postlarvae II (P_3)	84.3	94.8	95.2	0.0830
Juvenile (P_4)	96.4	97.0	90.6	0.2683
Overall survival [c]	53.8	51.6	72.3	0.0440

a/ Probability level of significance in survival of young walleyes among sources as determined by ANOVA.

b/ Underscore signifies no significant differences in mean response for the indicated stock source ($p < .05$; Tukey's multiple range test).

c/ Overall survival probability for a given stock is equal to $P_1 \times P_2 \times P_3 \times P_4$ where Pi is expressed as a decimal fraction for survival of offspring from each female.

Water chemistry at river intake during hatching experiments
(Auer and Auer, 1986)

Date	pH	DO (mgO_2/L)	NH_3-N (ugN/L)	NO_2-N (ugN/L)	H_2S (ug/L)
4/18	8.76	14.6	110	8	0.9
4/19	8.94	16.5	80	9	0.8
4/20	8.70	11.0	86	9	0.9
4/21	8.97	12.8	129	9	0.5
4/22	8.83	10.3	187	7	0.8
4/23	8.88	9.5	162	4	0.7
4/24	8.82	10.0	153	5	0.8
4/25	8.88	11.0	183	11	0.6
4/26	8.87	10.4	44	11	0.6
4/27	8.54	10.5	159	7	1.6
4/28	8.91	11.0	203	12	0.7
4/29	8.90	10.6	207	10	0.7
4/30	8.92	10.6	205	10	0.6
5/1	8.94	10.2	74	9	0.5
Mean	8.85	11.4	142	9	0.8

Chemical conditions at the sediment-water interface
(Auer and Auer, 1986)

24 June 1985 - Temperature = 22 °C

Station	pH	DO (mgO_2/L)	NH_3-N (ugN/L)	NO_2-N (ugN/L)	Sed. COD (mgO_2/gDW)	H_2S (ug/L)
1	7.45	6.6	105	48	12	9.7
2	7.22	5.9	289	64	41	16.6
3	8.23	5.3	143	54	16	3.3
4	8.11	6.4	99	55	24	3.6
5	7.65	0.2	817	68	183	43.8
6	7.39	0.5	1874	15	157	55.5
7	7.54	4.0	163	21	353	89.2
8	7.75	3.1	386	37	463	11.5
9	8.25	6.9	168	61	27	1.8
10	8.18	4.2	257	46	319	4.8

14 August 1985 - Temperature = 24 °C

Station	pH	DO (mgO_2/L)	NH_3-N (ugN/L)	NO_2-N (ugN/L)	Sed. COD (mgO_2/gDW)	H_2S (ug/L)
1	7.31	3.9	115	--	26	17.5
2	7.59	5.3	155	--	13	7.7
3	7.86	6.9	84	--	6	5.1
4	7.73	6.8	272	--	39	8.2
5	7.47	0.6	2339	--	224	189.9
6	7.49	0.9	2372	--	140	95.0
7	7.32	2.9	1778	--	375	289.9
8	7.36	1.5	5199	--	224	237.0
9	8.43	7.2	74	--	--	1.7
10	8.45	7.0	73	--	--	1.7

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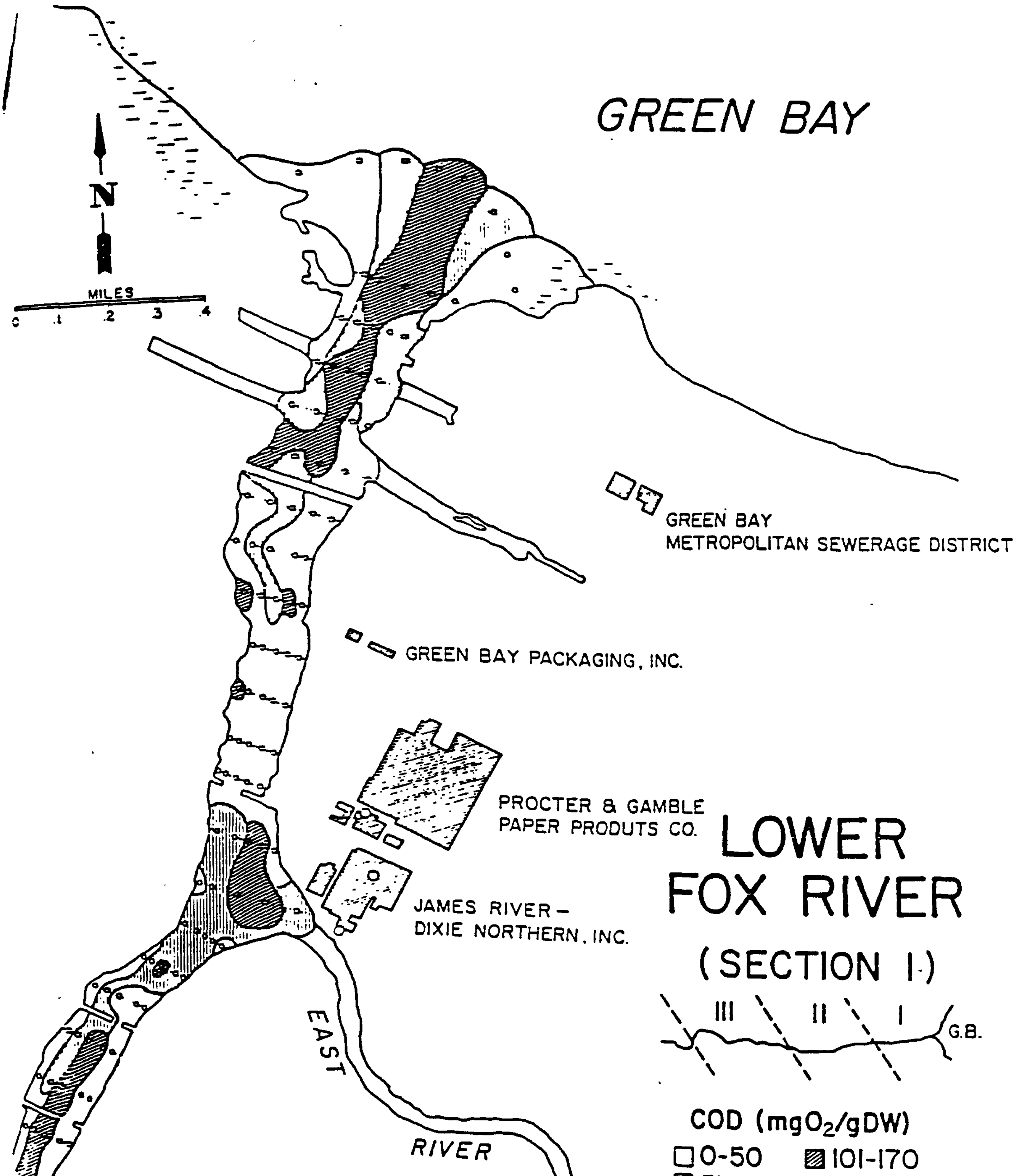

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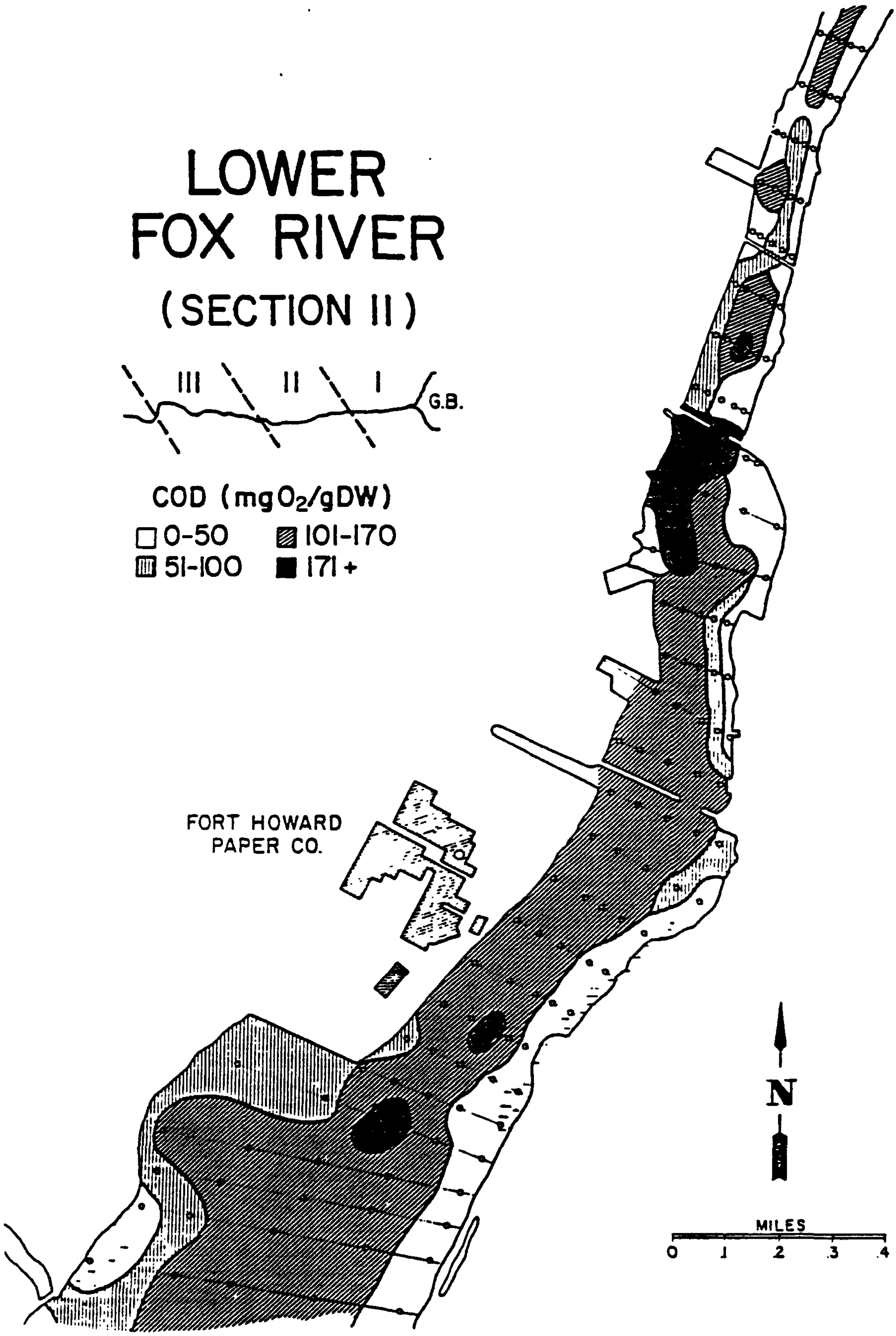

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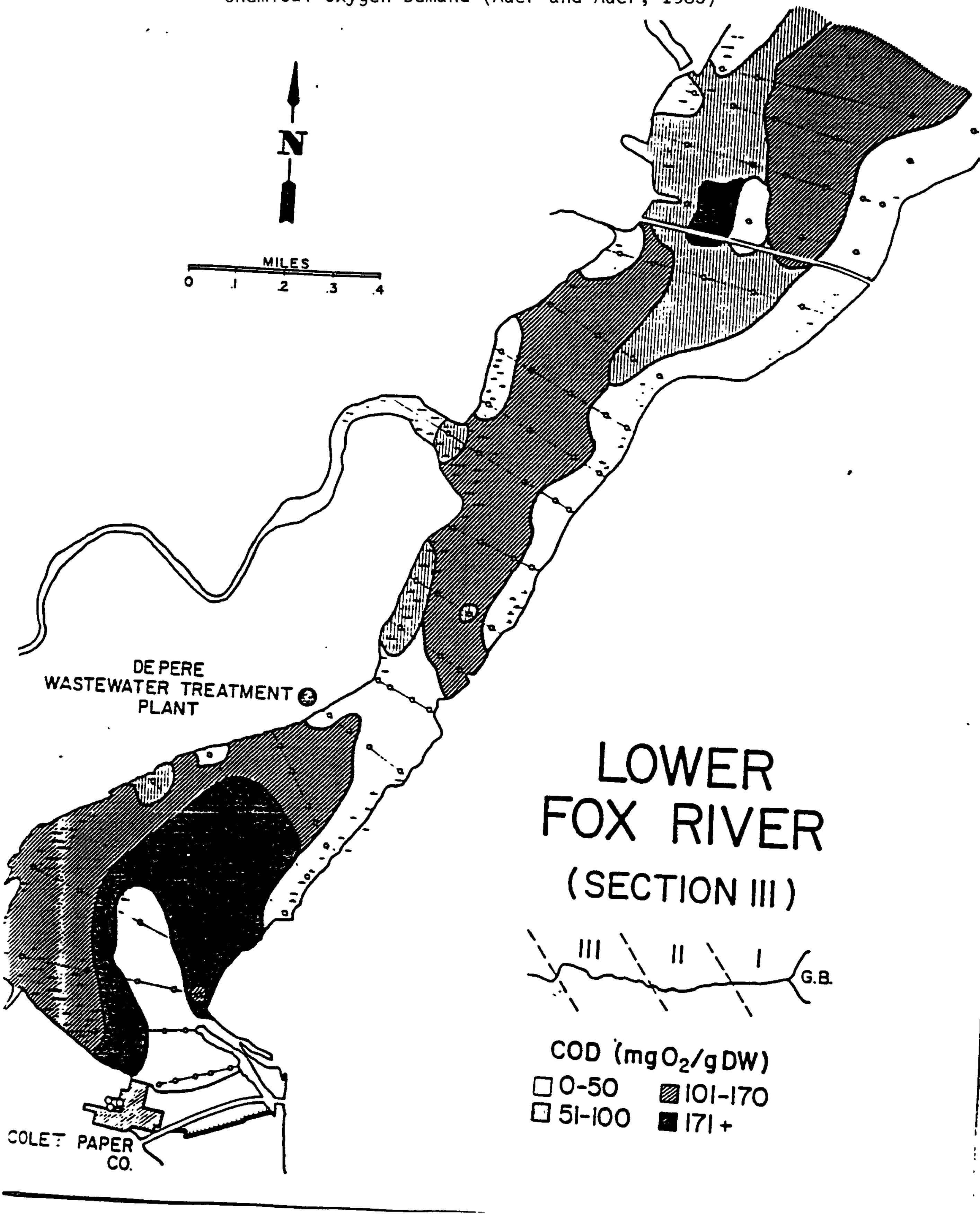

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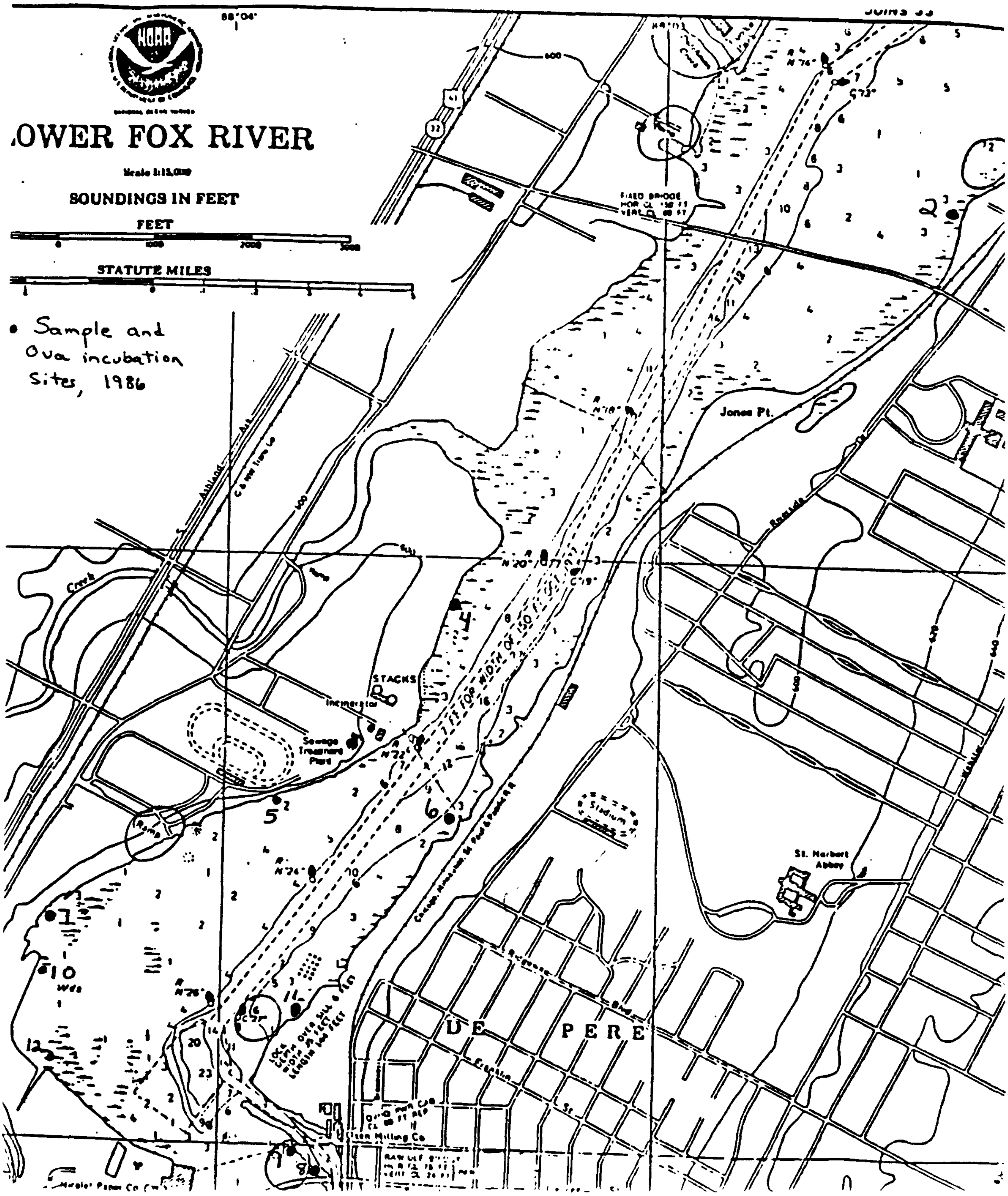

Survival of walleye ova incubated in non-groomed tissue culture triads during April 1986. (Average of all replicates and all females, uncorrected for initial ova viability). (Brooke et al., 1986)

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Abundance of Fish Species Caught by Fyke Nets in the Lower Fox River, April, 1985 (Balcer et al. 1986)

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Sauger (<u>Stizostedion canadense</u>)	4
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