WATER QUALITY INVESTIGATIONS IN THE UPPER SERPENT RIVER 1980-1984

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Ministry of the Environment

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CONCLUSIONS AND RECOMMENDATIONS

Because the Provincial Water Quality Objectives for ammonia are exceeded for the length of the upper Serpent River downstream of the industrial effluents during certain periods of the year, it is inappropriate to define mixing zones.

Due to the periodic presence of ammonia concentrations potentially lethal to fish, the immediate rehabilitation of the upper Serpent River is not a viable option with the existing process technology. It is recommended that the investigation of an alternate process technology that would significantly reduce in-stream ammonia concentrations be initiated.

Realizing that stress to fish communities exists periodically in the upper Serpent River from the interaction of ammonia and pH, it is recommended that a feasibility study into effluent pH control be initiated. This study should determine the effect of effluent pH maintenance in the 6.5 to 7.5 range, recognizing the implications to downstream ammonia oxidation and the mobilization of metals from tailings areas.

A study to define the cause of elevated river pH values during the winter months should also be initiated.

INTRODUCTION

The Ontario Uranium Mining Industry commenced in 1953 with the discovery of a large uranium-bearing ore body in the Serpent River basin. Sparked by a large uranium market, development proceeded rapidly, with eleven mines in operation by 1957.

A decline in the world uranium market reduced the number of operating mines to five by 1966. The continued uncertainty of markets further reduced mining activity in the Serpent River basin until, in 1972, only two mines were operating.

Surveillance of waste control operations in the Serpent River basin by Ontario began in 1957, with emphasis on containment of mill wastes and investigation of chemical pollution of receiving waters.

A major investigation of water quality and its associated biological impacts as related to mining activity in the Serpent River basin was carried out from 1966 to 1969. The findings of that study were documented in a report entitled "Water Pollution from the Uranium Mining Industry in the Elliot Lake and Bancroft Areas" (O.W.R.C., 1972).

In 1976, a Ministry study documented some improvement in the chemical water quality of the basin, notably a decline in $Radium^{226}$, ammonia, total dissolved solids and sulphate concentrations, and an increase in pH (Roy and Keller, 1976).

About 1974, a resurgence in the demand for uranium as a source of energy occurred. In order to meet long term sales commitments and an expanding market, Rio Algom and Denison Mines Limited proposed to increase their production facilities by expanding existing mines and rehabilitating others.

An Order-in-Council, dated September 22, 1976, directed the Environmental Assessment Board to evaluate the advantages and disadvantages to the environment of this proposed expansion. In May, 1979, the Environmental Assessment Board released its findings. Keynote were the following recommendations on water quality:

> "The Board finds the objective of restoration of the aquatic habitat in the Serpent River system to support a viable, self-sustaining, healthy and wholesome fishery to be appropriate.
>
> The Board finds that the levels established for pH (6.0 or above), ammonia (1.0 mg/L or below) and TDS (500 mg/L or below) are not unreasonable for the restoration of a fishery although serious attention must be paid to raising the pH to 6.5 or more, and lowering the ammonia below 1.0 mg/L.
>
> The Board recommends that a treatment program be developed for Quirke Lake by the mining companies to raise the pH by the addition of lime and sodium or calcium carbonate. The implementation of the program must be coordinated with ammonia reduction programs in the mine/mill facilities and care must be taken to avoid molecular ammonia toxicity."

Historically, Quirke Lake, the first lake downstream of mining-milling discharges, supported a lake trout (*Salvelinus namaycush*) and walleye *(Stizostedion vitreum vitreum)* fishery. By 1961, six uranium mines surrounding the lake had been in production for six years and interest in angling had apparently tailed off because of poor angling success. Investigations carried out by Duckworth (1977), documented an absence of game fish in Quirke Lake with contamination by the uranium mining industry strongly implicated as a contributing factor.

Although a good historical documentation of the fishery in the upper Serpent River is not available, the river is reported to have been utilized as a spawning area by the Quirke Lake walleye population. It also supported brook trout *(Salvelinus fontinalis).* (Purych-Bowman, personal communication).

Rehabilitation of the upper Serpent River and Quirke Lake to support a viable, self sustaining fishery is contingent on the presence of favourable water quality, food resources (benthos and forage fish) and suitable spawning habitat. Within the framework of these requirements, studies were undertaken during 1980 and 1981 in the upper Serpent River between Dunlop and Quirke Lakes to:

1) define effluent mixing zones in relation to the terms and conditions of the Ministry's Policy 5 on mixing zones (MOE, 1978).

2) document in-stream water quality; first under low summer flows in 1980 and subsequently in 1981 throughout the ice-free season.

3) determine the biological status of the river by assessing the benthic and fisheries communities.

4) investigate the acute effects of effluent discharges on fish, through laboratory bioassay techniques and the use of *in-situ* caging exposures.

Results of the studies are presented in the following sections of this report: Part I - Water Quality and Mix no Zone Studies, Part II - Biology, and Part III - Fish Bioassay Studies.

STUDY AREA DESCRIPTION

The study area of the upper Serpent River is shown in Figure 1. The Serpent River flows from a small dam at the outlet of Dunlop Lake (elevation 379.5 m) to Quirke Lake (elevation 363.5 m), over a distance of approximately 8 kilometres (km). Dunlop Lake is a typical oligotrophic Precambrian shield lake, supporting a mixed coldwater fishery. It is an important recreational lake for the area's residents.

The river enters Stollery Lake about 0.7 km below the Dunlop Lake outlet. This lake has been divided by an earth fill dam into two areas. The eastern portion receives overflow from the Denison Mine's Long Lake and Williams Lake tailings disposal areas, and is used as a settling pond following barium chloride treatment of the influent to precipitate radium. The western portion of the lake is approximately 3 metres (m) lower than the eastern portion and receives the drainage from the upper lake via a culvert at the northern end of the dam, as well as the flow from the Serpent River.

North of the Denison Mine Access Road, treated effluent from the inactive Williams Lake beaver pond area enters the river. Approximately 3.5 km downstream of Dunlop Lake, Bud Creek joins the Serpent River at the point where the river bends toward the east. Bud Creek drains the Quirke Mine tailings disposal area which receives tailings from Rio Algom's Quirke mill complex. There are no effluent discharges to the river between Bud Creek and Quirke Lake.

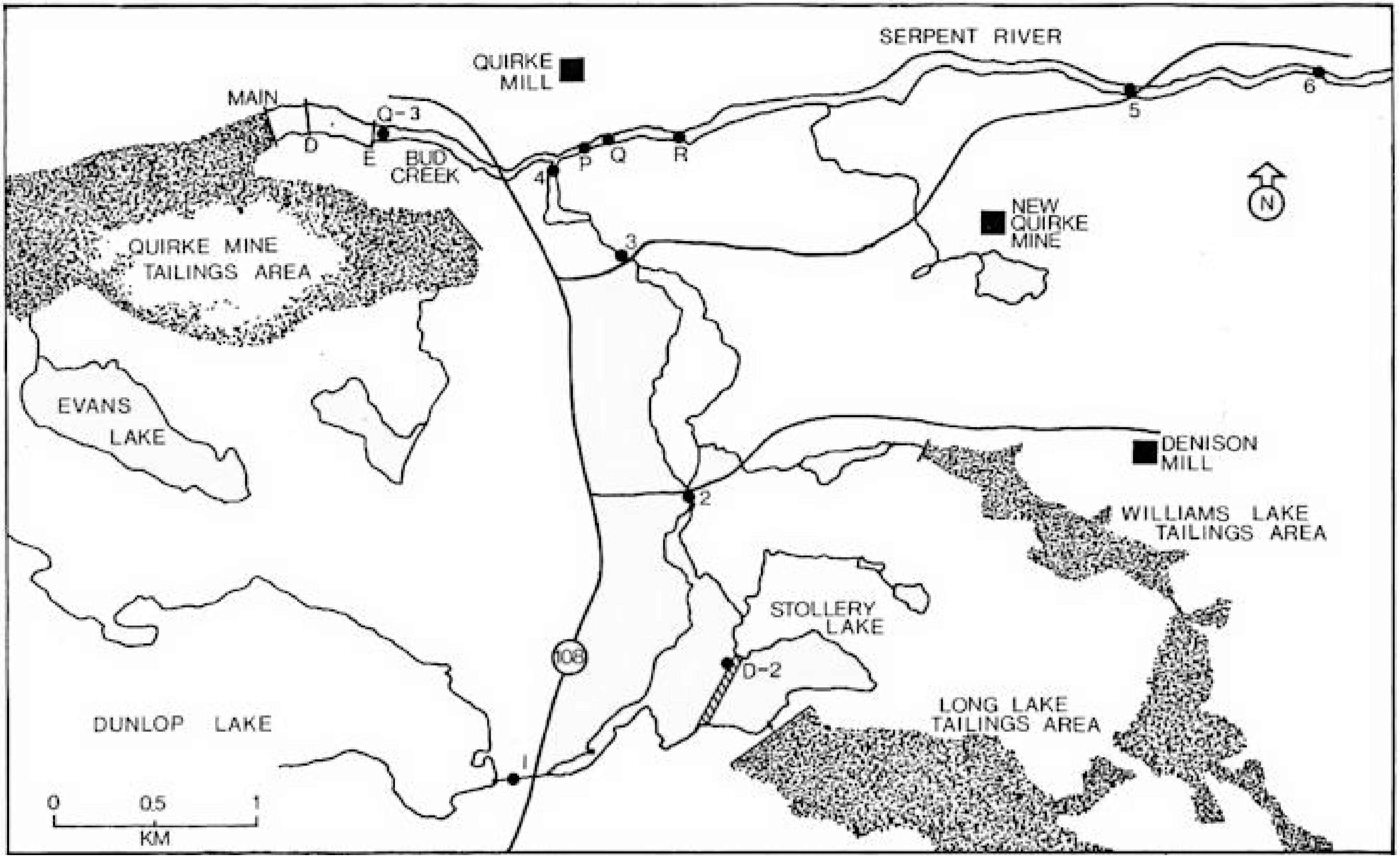

FIGURE 1 - Upper Serpent River System Study Area.

PART I - WATER QUALITY AND MIXING ZONE STUDIES

The objective of this part of the study was to define water quality conditions in the upper Serpent River with reference to the Ministry's Policy 5 on mixing zones (MOE, 1978).

When compared with Provincial Water Quality Objectives (P.W.Q.O.) and Ministry policy on mixing zone requirements, these data were expected to provide an indication of the overall suitability of the system for aquatic life and reveal to what extent the passage of fish might be restricted. In addition, the study would provide a data base useful for determining what level of effluent control would be needed to upgrade water quality to achieve the long-term goal of rehabilitating the system for spawning of resident fish species.

METHODS

On June 10 and July 23, 1980, chemical sampling was conducted at all stations between Dunlop Lake and Quirke Lake, and of the Stollery and Bud Lake tailings effluent sources (see Figure 1). Bud Creek (station Q-3) and Serpent River (station 3) flows were gauged. Water sampling was carried out along transects, at the confluence of each effluent source with the Serpent River in order to define chemical gradients in the mixing zone. At Stollery Lake, radial transects were established from the culvert into the lake. Samples were taken from the surface and from near the bottom along these transects. Below Bud Creek, three transects ("P", "O" and "R") were established across the stream over a distance of approximately 1.3 km. Also, samples were taken at station 4, immediately above the Bud Creek confluence. Samples were analyzed for pH., total dissolved solids (TDS), alkalinity, sulphate, chloride, ammonia, total Kjeldahl nitrogen, nitrite, nitrate, uranium, copper and zinc. Water samples collected for laboratory bioassays (see Part III) were analyzed for Ra^{226} and gross alpha and beta activity. Measurements of temperature, dissolved oxygen and conductivity were made in the field.

In 1981, with ammonia identified as the principal element of concern, a program of bi-weekly ammonia sampling was instituted at four stations (1 , 2, 3, and 6) from May to November.

RESULTS

(a) Main River Stations.

June and July 1980 water quality survey data for main river stations and effluents are summarized in Appendix A (Tables A-1 and A-4). Dissolved oxygen is not reported; however, spot measurements in thee field were greater than 8 mg/L throughout the study reach.

Water quality was excellent in the short section of the study area between Dunlop Lake and the inlet to Stollery Lake. The specific conductance values at the Dunlop Lake outlet (station 1) were in the 25-50 μmho/cm range. The concentrations of all variables were very low in comparison to those at downstream stations.

The discharge of tailings effluent from the Denison-Long Lake tailings area via Stollery Lake increased TDS concentrations at station 2 to 850 mg/L and 1290 mg/L during the June and July surveys, respectively. These concentrations exceed the 500 mg/L outlined by the Environmental Assessment Board (1979) as reasonable for the restoration of a fishery. $Radium^{226}$ and gross beta activity were less than the Provincial Water Quality Objectives (P.W.Q.O.), and the pH range was within the objectives. Un-ionized ammonia concentrations exceeded the P.W.Q.O. in July.

Station 3 had significantly higher concentrations than station 2 of all parameters except zinc.

At stations 5 and 6, P.W.Q.O. were met. for pH and Ra^{226}; however, un-ionized ammonia criteria exceeded the objective of 0.02 mg/L. Inputs from the Quirke Mine tailings area via Bud Creek resulted in slight increases in already elevated levels of un-ionized ammonia, nitrate, calcium, zinc and uranium.

(b) Mixing Zone Studies

Transect sampling results for the Stollery Lake and Bud Creek mixing zones are presented in Figure 2 and Table A-2 (Appendix A), respectively.

(i) Stollery Lake:

Conductivity levels in June, in the surveyed western part of Stollery Lake, were in the order of 1300 µmho/cm. The conductivity of the inflowing river water from Dunlop Lake was 43 µmho/cm. On the basis of spot measurements, the low conductivity Serpent River plume could not be discerned beyond the inflow to the lake.

The Long Lake tailings effluent to Stollery Lake was found to have a conductivity of 2800-3600 µmho/cm. Vertical profiles in the lake in the immediate vicinity of the discharge culvert showed increasing concentrations with depth for uranium, TDS, nitrate, ammonia and calcium. Surface water conductivity, uranium and ammonia gradients, represented by isopleths, are shown in Figure 2. Conductivity in this zone approaches average lake conductivity (1300 µmho/cm) a very short distance beyond the outfall.

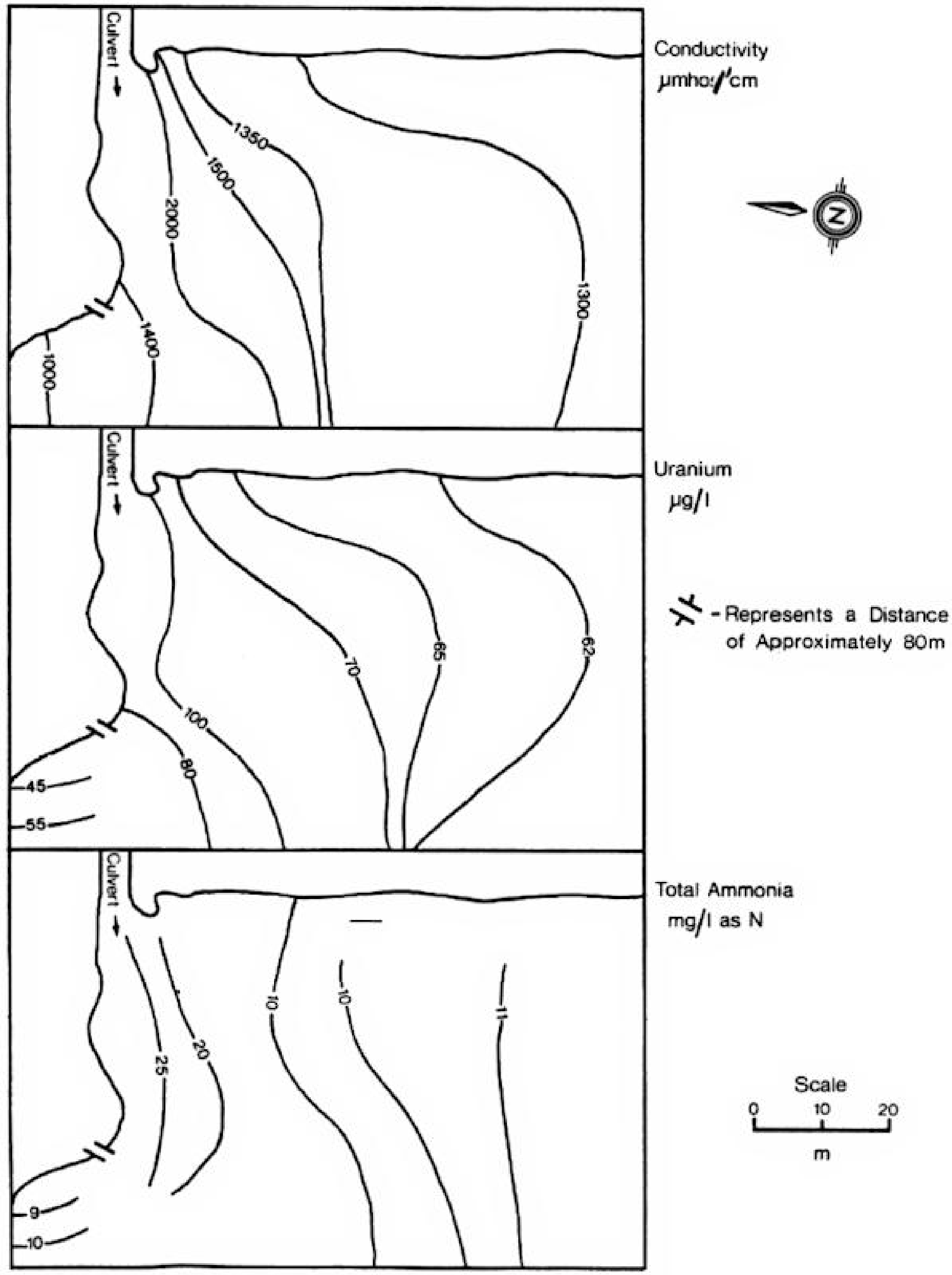

Figure 2 - Stollery Lake Mixing Zone.

(ii) Bud Creek:

The water quality data for this zone are summarized in Appendix Table A-2. Water quality sampling below the Bud Creek inflow indicated elevated concentrations of chemical variables at all points across transect P. Concentrations were slightly higher on the north (Bud Creek) side of the river. At transect Q and further downstream, concentrations were generally uniform across the channel. A decline in concentrations for both conservative and non-conservative parameters was also evident. These observations are illustrated in Figure 3 for total dissolved solids and total ammonia.

(c) Seasonal Changes in Un-ionized Ammonia Concentrations

The results of the 1981 ammonia monitoring program are summarized and presented in Figure 4. The individual pH, temperature and ammonia data used to derive these un-ionized ammonia concentrations can be found in the 1982 Ministry publication "Serpent River Basin, Water Quality Data, 1981".

By late June, un-ionized ammonia concentrations exceeded the P.W.Q.O. of 0.02 mg/L, in response to declining flows and increasing water temperatures. These concentrations remained elevated throughout the ice-free season and showed no seasonal decline with cooler water temperatures. Historical water quality monitoring data indicate that these un-ionized ammonia concentrations remain elevated throughout the winter months, reaching a maximum in January and February in response to high in-stream pH values.

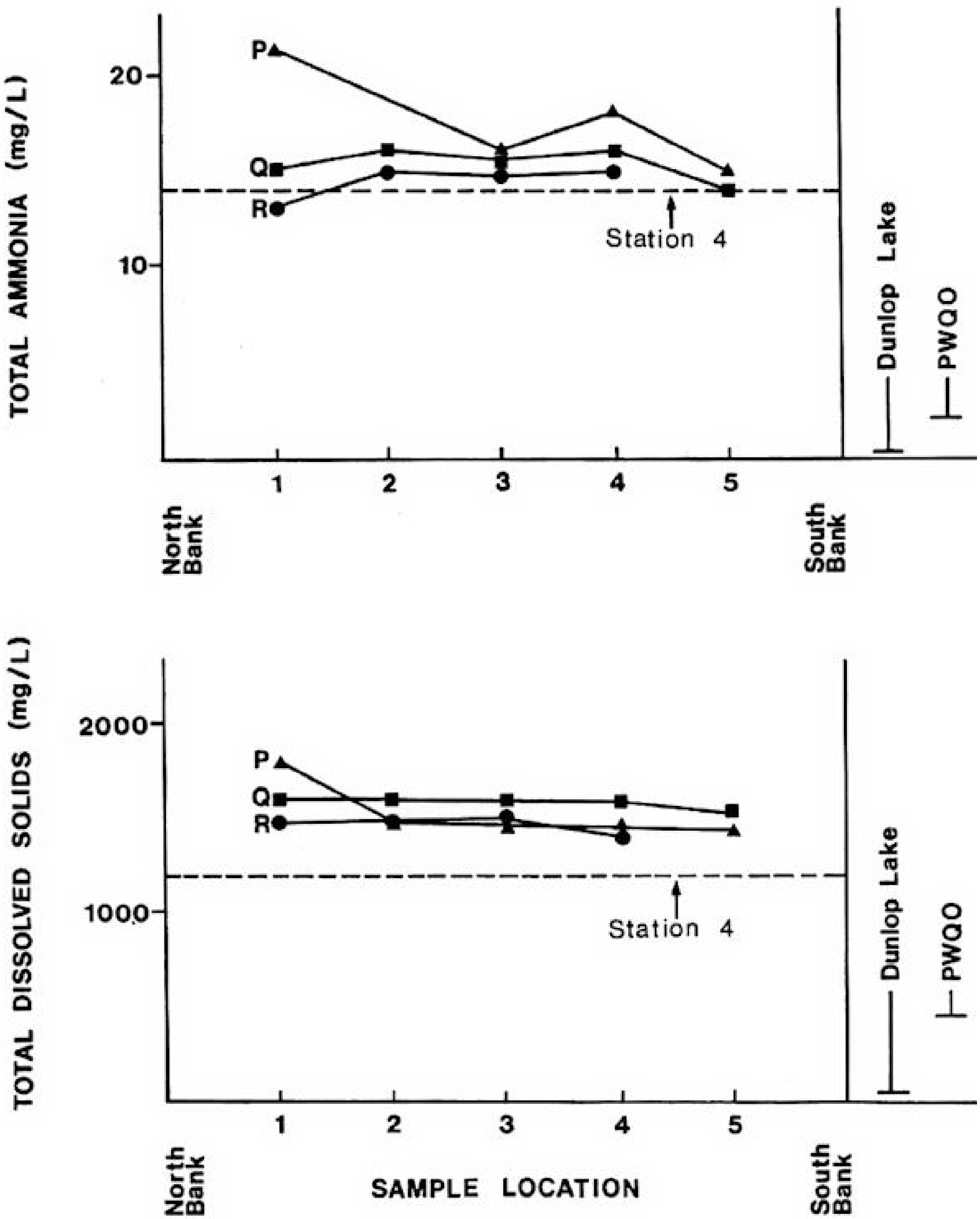

FIGURE 3. Cross-sectional Zone of Mixing Below Bud Creek For Total Ammonia And Total Dissolved Solids.

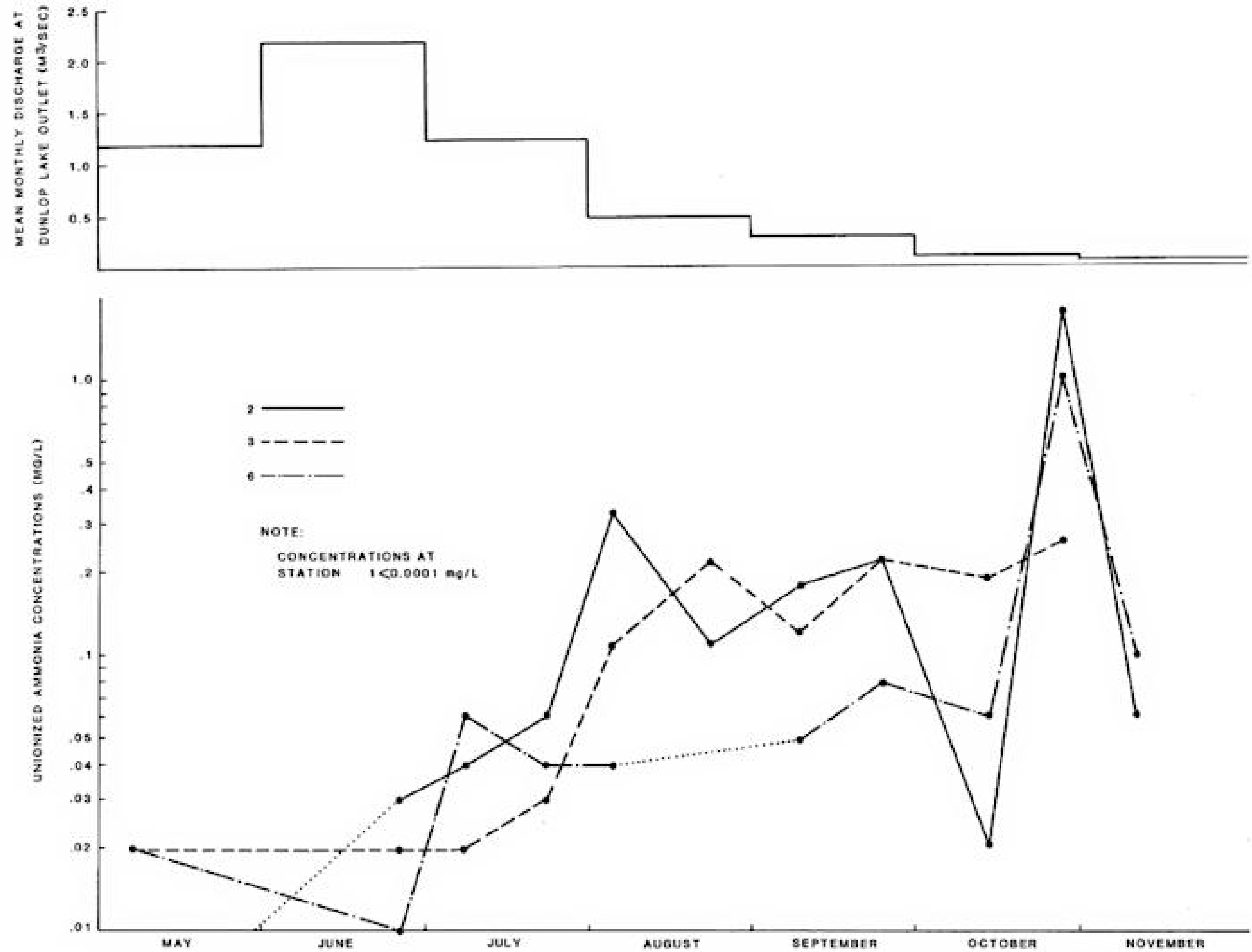

FIGURE 4. Seasonal Changes in The Concentration of Un-ionized Ammonia in The Upper Serpent River 1981.

DISCUSSION

Exclusive of those waters immediately downstream of Dunlop Lake, water quality is degraded for the entire study reach at certain times. Degradation is evident immediately below the inlet of the river to Stollery Lake.

Because of the relatively uniform distribution of pollutants at concentrations in excess of Provincial Water Quality Objectives throughout the lake, the two-dimensional descriptions associated with mixing zone and "zone of passage" concepts need not be applied. Rather, the entire cross-section of the waterbody in this area has to be considered as a high risk area to fish passage.

Un-ionized ammonia concentrations remote from the immediate area of the Stollery Lake outfall are in the 0.06-0.10 mg/L range at the surface and approximately twice this concentration at depth. These concentrations are above the threshold level for sub-lethal effects of ammonia on rainbow *trout (Salmo Gairdnerii)* (MOE, 1979).

Other pollutants potentially toxic to aquatic life such as copper and nitrite are present in elevated concentrations, with copper concentrations exceeding the P.W.Q.O. of 5 µg/L. Avoidance thresholds for this metal are reported as low as 2.6 to 15.5 µg/L (Giattina *et al*, 1982). At the observed concentrations of nitrite, some acute toxicity might be expected.

The aggregate ecological effect of all pollutants on potential resident and spawning fish is difficult to assess. Parts II and III of this report address this question more directly. Based on concentrations of un-ionized ammonia alone, the river appears marginal for the survival of a fishery.

Figure 3 shows the effect of the Bud Creek effluent on the Serpent River below station 4, using TDS and total ammonia as representative parameters. Concentrations at the

Dunlop Lake outlet are included for comparison. It is evident that at station 4 just above Bud Creek, pollutant concentrations are still high as a result of the Stollery Lake inputs. During the 1980 survey the Bud Creek plume further elevated concentrations of all parameters and was found to be mixed completely across the stream within 300 metres of the confluence. Mass balances indicate that even with no upstream effluent inputs, the Bud Creek source would result in river concentrations for several parameters well in excess of P.W.Q.O. under most existing flow conditions.

Although some decay of ammonia and loss of dissolved solids is apparent, the impact of Bud Creek extends to the downstream limit of the study area at station 6. Part of the solids loss (also noted for uranium) may be attributed to adsorption-settling processes in this reach. Heavy siltation was noted just below station R where a railroad track crosses the river and flow is restricted by four culverts under the trackbed.

With respect to mixing zones, the following conclusions may be drawn:

(1) The zone of mixing of the Denison tailings effluent to Stollery Lake extends to about 100 metres away from the effluent culvert.

(2) The zone of mixing of the Rio Algom effluent discharged via Bud Creek extends to transect P (approximately 300 metres).

(3) At the downstream boundary of both mixing zones, concentrations of un-ionized ammonia are well in excess of P.W.Q.O. In the case of the Bud Creek effluent discharge, excessive levels would also be expected at the periphery even without the influence of the upstream Stollery Lake discharge.

PART II - BIOLOGY

The objective of this component of the 1980 and 1981 studies was to determine the status of the biological communities of the upper Serpent River by assessing benthic and fish taxa throughout the study area.

METHODS

Triplicate Surber samples were taken in late July, 1980, at stations 1,2,3 and 6. Additional qualitative samples were collected at each station using a hand sieve and bucket. Supporting information on land use, substrate, water temperatures and the presence and relative abundance of aquatic vegetation was collected and recorded at the time of the benthic survey. A comparison of benthic macroinvertebrate data from this survey was made with data collected in 1967 and 1968 (O.W.R.C., 1971), to determine if any significant changes in community structure had taken place.

Fish communities were assessed in August, 1981, subsequent to the sighting of spawning white suckers *(Catastomus commersonii)* during the spring of that same year. At stations 1, 2, 3 and 6. 100 m reaches of comparable habitat were sectioned off using 30 m seine nets. These reaches were then intensively electrofished for 70 minutes using a Smith-Roote model VII electrofisher.

RESULTS

A description of the biological and physical characteristics of the four river stations is contained in Table B-1 (Appendix B). The numbers and types of benthic fauna at each station are listed for each Surber sample in Table B-2. These results are summarized and presented in Figure 5.

Macroinvertebrate communities at station 1, the upstream reference station, were typical of a coolwater environment with good representation by pollution intolerant stoneflies and caddisflies (Table B-2). Standing crop estimates, based on counts of individuals/m^2, were high for the dilute waters of the shield as compared to those reported in similar, non-impacted environments (Keller and Sale, 1982).

Although a significant difference in standing crop was evident between stations ($F=23.2$, $p<0.05$), there were no differences between the numbers of taxa per station ($F=344$, $p>0.05$). Some station-to-station differences in the presence or absence of specific taxa were apparent.

At station 2, downstream of the Stollery Lake effluent discharge, benthic standing crops showed a slight increase, while numbers and types of pollution intolerant taxa showed a slight decline. This was indicated by the loss of two genera. each of stoneflies and caddisflies. At station approximately 1 km downstream, an 80 percent (%) cover of benthic algae was noted on the instream substrate.

Macroinvertebrate community composition was similar to that of station 2. A slight increase in the number of pollutant intolerant taxa was apparent, as well as an increase in total numbers.

At station 6, several km below the Bud Creek inflow, the water was notably grey and a heavy benthic growth (100% cover) was observed on the substrate. Standing crop and diversity of the macroinvertebrate community showed marked declines relative to station 3.

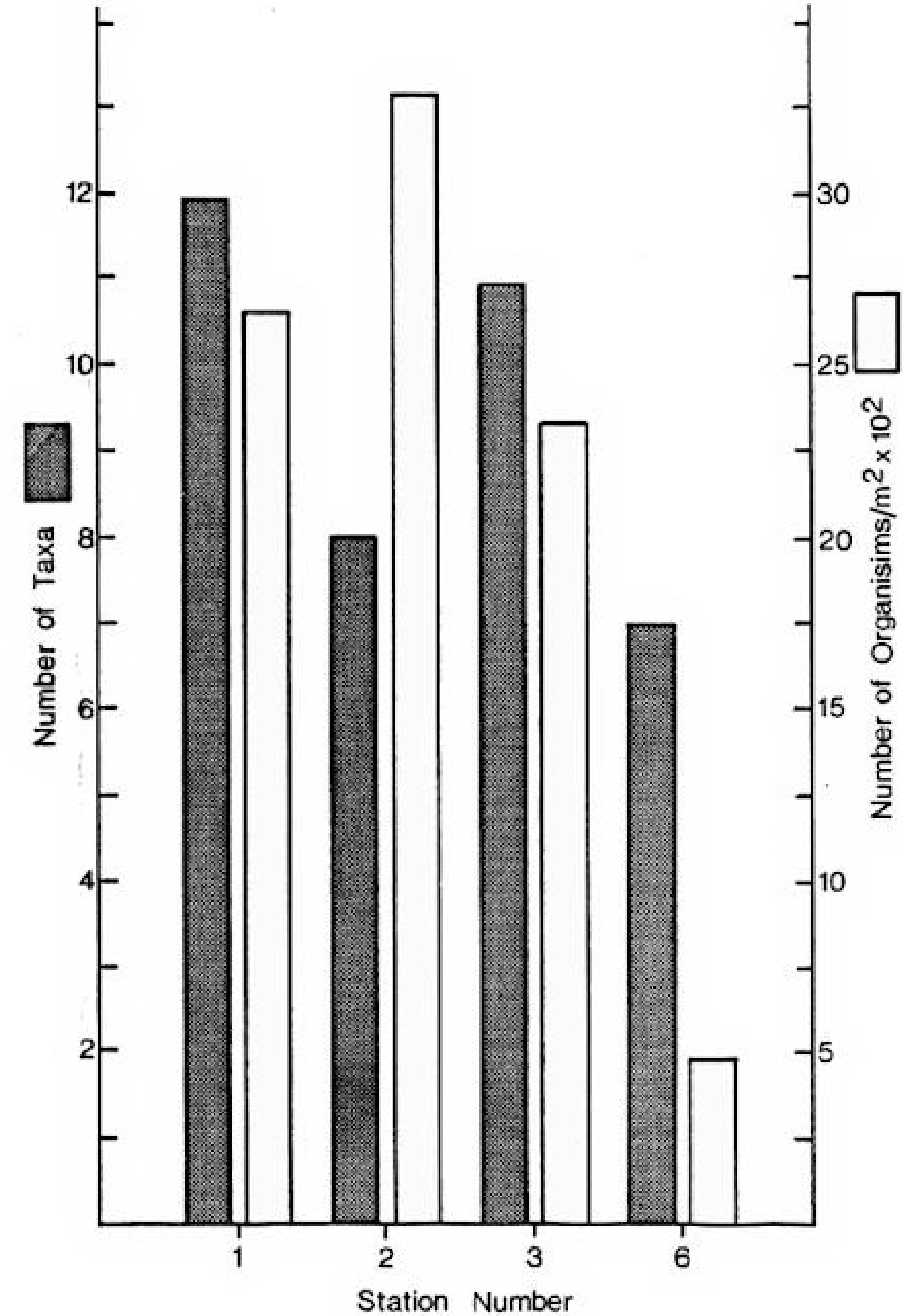

FIGURE 5. Average Number of Taxa and Organisms/m^2 from the Upper Serpent River, July 1980.

Appendix Table B-3 presents historical invertebrate data. collected during 1967 and 1968. Comparing the historical and 1980 invertebrate data and allowing for differences in seasonality and sampling technique, very little change in the invertebrate fauna is apparent.

Diversity, as measured using Margalef's Index, was unchanged (see Table 1).

TABLE 1: Historical Comparison of Diversity (measured by Margalef's Index) for Two Stations on the Upper Serpent River.

STATION	MONTH/YEAR			
	June/67	July/67	May/68	July/80
1	1.5	3.7	2.7*	1.1, 1.5, 1.2, 3.2*
6	0.7	1.0	-	1.1, 0. 7, 1.5, 2.2*

* Surber plus qualitative sample; all other indices based on single Surber sample

Margalef's Index = $(S-1)/\text{Log}_{10}$ N where S is the number of taxa and N is the number of organisms/m^2.

During the August, 1981 electrofishing survey, no fish were captured at any of the stations, except station 6, where a few creek chub, (*Semotilus atromaculatus*, were captured. Qualitatively, bank and in-stream cover was rated poor to fair throughout the study reach, with the limit of upstream fish migration established by a natural 2 m high falls just upstream of station 2 (the Denison Mine access road).

DISCUSSION

Benthic macroinvertebrates throughout the reach from Dunlop Lake to Quirke Lake reflected only moderate water quality impairment associated with the two major waste discharges at Stollery Lake and Bud Creek. Relatively minor shifts in community composition and a general decline in standing crops with distance downstream were apparent. Overall, standing crops of benthic macroinvertebrates were judged to be high, relative to the normally dilute and thus less productive waters of the Precambrian shield. The organisms present, notably the caddisflies, were judged to be present in sufficient numbers to provide a food base capable of supporting a fishery.

Present-day macroinvertebrate communities are similar to those documented in the upper Serpent River during the late 1960's.

The results of the August, 1981, electrofishing survey suggest that a forage fish population is not present in the upper Serpent River. The lack of fish is attributable to the seasonally elevated ammonia concentrations (see Part I).

PART III - FISH BIOASSAY STUDIES

The objectives of the bioassay component of the 1980 and 1981 studies were:

(1) to investigate the acute effects on fish of the mine/mill effluents discharged to the upper Serpent River.

(2) to determine the factor(s) limiting survival in these effluents by selectively reducing or altering specific chemical components under controlled conditions and observing the effects on fish lethality.

(3) to determine, using *in-situ* caging techniques, whether fish could survive a short term exposure in the river during the spring.

METHODS

(a) Rainbow Trout Bioassays

During 1980, static laboratory bioassays (96 hr.) were performed to assess the acute lethality of the mine/mill effluents, D-2 and Q-3, to rainbow trout fingerlings. A dilution series of each effluent was prepared with dechlorinated Toronto tap water to determine what concentration would produce mortality in 50 % of the test fish (a 96 hr. - LC_{50}). Test water was aerated. Bioassays were conducted at 15°C with 10 fish/test solution.

Because ammonia concentrations in the effluents were considered to be the primary toxicant, subsamples of the effluents were passed through clinoptilolite resin to reduce ammonia levels (U.S.E.P.A., 1971). Bioassays and chemical analyses were performed on samples before and after treatment to determine the contribution of ammonia to the toxicity of the waste.

A second set of bioassay samples was collected in August, 1980, for comparative purposes. A pH adjustment on a portion of the D-2 sample (Denison Mines effluent) was undertaken to assess the effects of pH reduction on effluent toxicity. The pH was adjusted from a level of 10.0 to 7.8 using 10% HCl. In addition, bioassay samples were obtained from the Rio Algom, Panel Mine effluent which contains significantly lower ammonia concentrations due to a different process technology.

(b) Zebrafish Hatchability Tests

An egg hatchability and fry survival study with zebrafish *(Brachydanio rerio)* was undertaken using effluents D-2 and Q-3; river samples from sites F-1, F-3 and F-5 (all of which were collected August 20th); and dechlorinated Toronto tap water (the laboratory control). The eggs were supplied by laboratory-reared breeding adults and were randomly placed in the test containers, exposure commencing within 6 hours after the initial spawning.

Each sample was tested in duplicate at 25-26°C with 15 eggs per 500 ml test container (actual river temperatures at the time of sampling were 22°C). The test solutions were replaced every 48 hours and swim-up fry were fed Paramecium in proportion to the number of individuals in the test container. Hatchability and organism mortality levels were measured at the various developmental stages (pre-eyed egg, eyed egg, sac fry, swim-up fry) during the study. The test was terminated 7 days after the last hatch.

(c) *In-situ* Exposures

Exposures of brook trout were undertaken during May 4-8, 1981, along the upper Serpent River between Dunlop and Quirke Lakes (Figure 6). The test fish were 6-11 g fingerlings from the Ministry of Natural Resources, North Bay hatchery, and the exposure cages were modified polyethylene minnow traps.

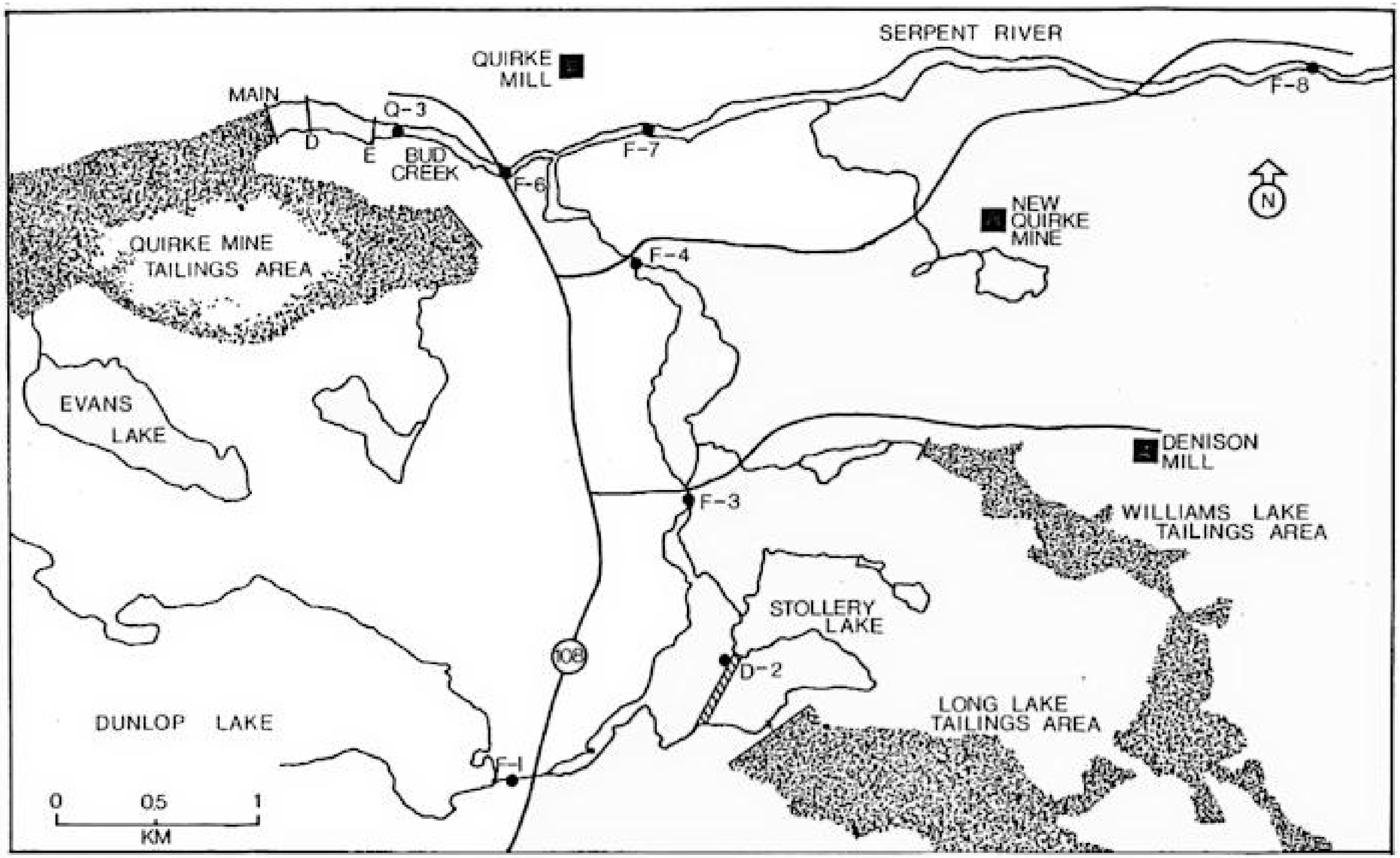

FIGURE 6. Upper Serpent River *In-situ* Fish Exposure Sites.

The trout were transported to the test site in polyethylene bags containing hatchery water and an oxygen headspace. At the study site, the water temperature of each bag was allowed to equilibrate to the river temperature prior to release of fish into the cages. No pre-exposure acclimation was undertaken at the site due to the similarity of hatchery and exposure water temperatures. The pre-exposure water temperature at the hatchery was 10°C, while the range of mid-day water temperatures at the exposure sites during the five successive days of the test was 10.0-16.0, 6.5-12.5, 9.0-14.0, 8.0-10.0 and 8.5-12.0°C, respectively.

Ten fish were exposed at each test site, except at the reference station F-1, where forty fish (10 fish/cage) were exposed. During the second day of the study, a cage of fish was transferred from the control site to the Denison Mine effluent discharge (D-2), in order to confirm the results of the previous day.

The fish were observed throughout the daylight hours of the test and the dead fish were removed from the cages. Water samples were collected daily from each exposure site for chemical analysis at the MOE laboratory in Toronto. On-site water analyses at each exposure site included daily oxygen and pH measurements, while water temperatures were taken twice daily.

Table 2. Toxicity Test Results — Denison And Rio Algom Effluents.

Company / Sample Location: Denison Mines — Elliot Lake

Station	SAMPLE			TEST		
	Name	Type	Date	Resultant 96-hr.LC_{50}	Type	Reference No.
D-2	Stollery Lake Dam	Grab	June 10/80	65%	---	S-70
D-2	Stollery Lake Dam - Treated (in-lab)	Grab	June 10/80	Non-lethal	Clino-treated	S-73
D-2	Stollery Lake Dam	Grab	Aug.20/80	20%	---	S-100
D-2	Stollery Lake Dam - Treated (in-lab)	Grab	Aug.20/80	>100% (30% mortality @ 100%	pH adjusted	S-103

Company / Sample Location: Rio Algom Mines — Elliot Lake

Station	SAMPLE			TEST		
	Name	Type	Date	Resultant 96-hr. LC_{50}	Type	Reference No.
Q-3	Bud Lake Creek. Dam E	Grab	June 10/80	48%	---	S-71
Q-3	Bud Lake Creek Dam E -Treated(in-lab)	Grab	June 10/80	Non-lethal	Clino-treated	S-72
Q-3	Bud Lake Creek Dam E	Grab	Aug.20/20	59%	---	S-101
	Panel Mine	Grab	Aug.20/80	>100% (40% mortality @100%	---	S-102

RESULTS

(a) Rainbow Trout Bioassays

The tailings pond effluents from both Denison Mine's Long Lake (Stollery Lake D-2) and Rio Algom's Quirke Mine (Bud Creek Q-3) tailings disposal areas were lethal to fish in June, 1980. There was complete fish mortality in the full strength effluent solutions and no mortality in test solutions of 40% or less. The 96 hr.- LC_{50}'s (concentrations lethal to 50% of the test fish over a 96 hr. test) were 65% v/v for the Stollery Lake sample and 48% v/v for the Bud Creek samples (Table 2).

Total ammonia concentrations in the two tailings effluents (Table A-3) were four times greater than the MOE mining effluent guideline of 10mg NH_3-N/L (MOE, 1981), and the amount calculated to be present as un-ionized ammonia exceeded values known to be lethal to fish (U.S.E.P.A., 1976). An un-ionized ammonia LC_{50} for rainbow trout fry of 0.2 mg/L has been reported by Liebmann (1960), while the LC_{50} for fingerlings has ranged from 0.6 to 1.4 mg/L at the Ministry's toxicity laboratory. In this study, the calculated levels of un-ionized ammonia at the corresponding LC_{50} values for the Stollery Lake dam (65% v/v) and Bud Creek (48% v/v) samples were 1.9 and 1.1 mg/L, respectively.

Undiluted samples of both clinoptilolite treated effluents were non-lethal to the test fish. Chemical data for the treatments are presented in Appendix Table A-3.

Clinoptilolite treatment reduced effluent ammonia concentrations to 1 mg/L from 43-44 mg/L. Calculated un-ionized ammonia concentrations were <0.01 mg/L, lower than the P.W.Q.O. of 0.02 mg/L. Prior to clinoptilolite treatment, effluent nitrite concentrations were also approaching potentially lethal values. The Stollery Lake and Bud Creek samples contained 8.0 and 3.3 mg/L as N, respectively. However, the buffering of effluents by the addition of $Ca(OH)_2$ for pH adjustment offset the potential nitrite toxicity. Wedemeyer and Yasutake (1978) found that an increase in hardness from 25 to 300 mg/L (as $CaCO_3$) increased the 96 hr.- LC_{50} for rainbow trout from 0.5 to 10.3 mg/L NO_2-N. Effluent hardness determinations were well in excess of 1000 mg/L as $CaCO_3$ (Table A-3).

The elevated calcium concentrations in the effluents are the result of $Ca(OH)_2$ treatment by the mills to raise the effluent pH prior to discharge. Although these additions have a positive effect on mitigating potentially lethal nitrite concentrations, the resulting increase in pH creates a shift in equilibrium, increasing concentrations of un-ionized ammonia, with a resultant increase in effluent lethality.

The clinoptilolite treatment increased sodium and aluminum levels in the effluents due to the ion-exchange properties of the resin. It is unlikely that these changes had a major influence on the decrease which was observed in the sample toxicity. Reductions of other parameters due to the treatment were observed as well. In both effluent samples, copper was reduced from levels of 0.020 mg/L prior to the treatment (pH 8.3-8.4; hardness 1500-1600 mg/L as $CaCO_3$). However, these pre-treatment levels are still 26 times lower than ones reported as lethal to rainbow trout (0.52 mg/L Cu, pH 8.0, hardness 371 mg/L as $CaCO_3$) by Howarth and Sprague (1978). Therefore, copper (and all other metal) concentrations appear to have been of little consequence in either pre- or post-treatment lethality levels. Copper concentrations in both effluents did however exceed P.W.Q.O. (5 µg/L) by a factor of four.

A second set of effluent samples collected -from the Stollery Lake dam and Bud Creek in August, 1980, were also lethal with LC_{50}'s of 20 and 59% v/v, respectively. The Bud Creek result was consistent with the test undertaken in the spring, while the Stollery Lake dam sample was significantly more toxic than that tested in June.

In addition to high ammonia concentrations of 19.7 mg/L, the August, 1980, Stollery Lake effluent pH of 10 units exceeded the range considered harmless to fish (6.0-9.0 units). Therefore, pH may have contributed to the lethality of the full strength effluent solution. Dilution of the effluent resulted in a bioassay pH of 8.7 and an LC_{50} of 20%

v/v. The calculated un-ionized ammonia concentration was 0.6 mg/L which is above levels known to be lethal to fish (Liebmann, 1960).

In-lab pH adjustment of the full strength effluent to a value of 7.8 units reduced lethality to 30%. The calculated un-ionized ammonia concentration was 0.4 mg/L which is considered to be marginally lethal.

During August, 1980, samples were collected and tested from the Panel Mine tailings area, representative of a mill employing the LAMIX (Limestone-Acid-Magnesia-Ion Exchange) process for uranium extraction, as contrasted to the Denison and Quirke Mills which employ a nitrate elution and ammonia precipitation process (NEAP).

Since the pH of the Bud Lake effluent (pH = 8.3) was close to that of the Panel Mine (pH = 8.9) the Bud Lake results are discussed here for comparative purposes. Metal concentrations in the two samples were in the same general range; however, the ionic strength of the Panel mill effluent was approximately two thirds of that from Bud Lake (Table A-5). Total ammonia (as N) was nearly 10 times greater in Bud Creek (39.1 mg/L) versus the Panel Mine effluent (3.4 mg/L).

Calculated un-ionized ammonia concentrations in the Bud Creek sample were 1.0 mg/L at the 96 hr.- LC_{50} (59% v/v). The corresponding concentration in the Panel mill effluent was 0.8 mg/L at its LC_{40} (i.e. 40% mortality occurred in the full strength solution). Lethality was reduced in the LAMIX process effluent due to substantially lower concentrations of ammonia.

(b) Zebrafish Hatchability Tests

Egg mortality in the pre-eyed life stage showed no differences between the effluent, river and control samples (Table 3); however, differences began to appear among samples in the eyed-egg stage. Mortality rates declined in the river samples and increased in the effluent samples. There was a great difference in mortality results of the "duplicates" for the Stollery Lake Dam (D-2) effluent during the eyed-egg stage. Unfortunately, no definite reason can be given for these differences.

Hatching success was highest for the test control (Toronto tap water) and the station 3 river samples, while levels in the Dunlop Lake outlet (sample control) matched those in the other Serpent River sample (station 5), with a 73% success rate. Hatchability in the effluents was lower with Stollery Lake (D-2) and Bud Lake Dam (Q-3), having only 33% and 50% hatching success levels, respectively. (Sample chemistry is presented in Appendix Table A-5.)

All organisms in the effluent samples which survived the hatch died within two days, while still in their sac fry stage of development. Survival of fry in the river samples matched or surpassed results for the controls.

(c) In-situ Exposures

The results of the May, 1981, in-situ bioassay (Figure 6) are presented in Table 4. Supporting water chemistry data are presented in Appendix Table C-1.

When the laboratory was unable to provide verifiable NH_3 results, concentrations were estimated by linear regression incorporating Kjeldahl nitrogen-nitrate and nitrite relationships. All measured and calculated NH_3 values, r values and linear equations are presented in Appendix Table C-2.

Although the effluent exposures exhibited variable lethality, no lethality or indications of stress were observed for the fish exposed at various sites throughout the river. The highest calculated value of un-ionized ammonia at a river site (F-7) was approximately ten times lower than required to produce acute lethality. Therefore it appears that a zone of passage for fish would have existed along the length of the upper Serpent River at the time of the *in-situ* bioassay.

Table 3. Zebrafish Hatchability and Mortality Levels of Different Life Stages Exposed to Serpent River Water and Mine Tailings.

SAMPLE		% HATCHABILITY	% MORTALITY										
Station	Description	Average from duplicates	Pre-eyed Egg		Eyed Egg		Sac Fry		Swim-ups		Total		Avg.
			A	B	A	B	A	B	A	B	A	B	
D-2	Stollery Lake Dam (Long L.) Effluent	33	27	27	73	7	0	66	--	-	100	100	100
Q-3	Bud Creek Dam (Bud L.) Effluent	50	13	27	47	13	40	60	--	-	100	100	100
1	Dunlop Lake - Control	73	13	33	7	0	0	0	0	7	20	40	30
3	Serpent River at Panel Mine Access Rd.	97	0	37*	13	0	7	0	0	0	20	37*	20
5	Serpent River Below Bud Cr.	73	27	20	7	0	0	0	0	0	34	20	27
	Dechlorinated Toronto Water Control	97	13	13	0	0	0	0	13	0	26	13	20

* Due to heavy egg fungal infestation in test beaker B the data from that beaker are not included in the average values outlined in this table.

Table 4. Fish Exposure Mortality Results and Associated Un-ionized Ammonia Concentrations.

EXPOSURE SITES [1]		PERCENT MORTALITY AT:			UN-IONIZED AMMONIA (mg/L) at:		
No.	Description	0 hrs	24 hrs	96 hrs	0 hrs	24 hrs	96 hrs
F-1	Reference	0	0	0	0.3×10^{-4}	0.4×10^{-4}	0.4×10^{-4}
D-2	Stollery Lake Effluent Decant	100 (at 1.5 hr)	--	--	4.63	---	---
D-2	Stollery Lake Effluent Decant[2]	100 (at 2 hr)	--	--	4.62	---	---
F-3	Serpent River, Denison Mine Access Road	0	0	0	0.01	0.003	0.01
F-4	Serpent River, Panel Mine Access Road	0	0	0	0.003	0.003	0.007
Q-3	Bud Creek, d/s Dam E	0	40	80	0.67[3]	0.62[3,4]	0.19
F-6	Bud Creek, at Hwy 108	0	10	50	0.74[3]	0.15[3]	0.25
F-7	Serpent River, d/s Bud Creek	0	0	0	0.03[3]	0.01	0.04[3]
F-8	Serpent River, at Federal Gauge	0	0	0	0.03	0.02	0.02

1 Refer to numbered locations on Figure 6
2 Second exposure undertaken 24 hrs. after the initial result.
3 Estimated values - see Chemical Sampling Methods Section and Appendix C
4 At 48 hrs. - NH_3 value was estimated to be 1.39 mg/L.

The effluent at Stollery Lake (site D-2) was very toxic, 100% mortality occurring after only 1.5 hours. A repeat of this exposure the following day produced similar results.

In contrast, at Bud Creek (site F-6), only 50% mortality occurred during 96 hours. The levels of total ammonia-nitrogen discharged from those two tailings areas (D-2 and Q-3) were not significantly different over 5 days ($p>0.05$), while there was a significant difference ($p<0.05$) in pH. In turn, the higher pH (of approximately one pH unit) at the Stollery Lake Dam produced un-ionized ammonia levels which were ten times higher than those at the Bud Creek culvert (F-6). The mean un-ionized ammonia levels (R ± S.D.) were 5.4 ± 1.0 versus 0.41 ± 0.2 mg/L for the two sites, respectively.

The concentration range of un-ionized ammonia (0.25-0.74 mg/L) at the Bud Creek site is comparable to levels cited in the literature as lethal to fish. Laboratory experiments have demonstrated that lethal concentrations for a variety of fish species are in the range of 0.2 to 2.0 mg/L, with trout being the most sensitive species (U.S.E.P.A., 1976). The ten times higher un-ionized ammonia levels at the Stollery Lake Dam discharge versus those at Bud Creek account for the differences in the lethal response time between the two sites (i.e. an LC_{50} in <1.5 hrs. vs. 96 hrs.). The upstream Bud Creek sample (Q-3) had large fluctuations in un-ionized ammonia levels (0.02-1.37 mg/L), due to flow pattern changes of a nearby creek during a storm event, and is not considered representative of the effluent from Dam "E".

DISCUSSION

The results of the fish bioassay studies revealed that the final effluents from Denison Mine's Long Lake and Rio Algom's Quirke mill tailings were lethal to test organisms. Elevated concentrations of ammonia compounded by high pH values were identified as the primary agents responsible for toxicity.

In-situ and laboratory experiments on river water show that fish survival in the upper

Serpent River is possible during certain periods of the year. A species of fish sensitive to ammonia such as the brook trout can survive under high flow, freshet conditions. However, low flow, high temperature conditions present in the summer and high pH and ammonia concentrations during the winter will create a greater possibility of fish mortality during those seasons.

SUMMARY

The zones of effluent mixing as described in Part I of this report are relatively small in size. The Stollery Lake zone of mixing extends approximately 100 metres from the point of discharge, the lake being about 850 metres wide at that point. Adjacent waters in Stollery Lake and the upper Serpent River upstream of Bud Creek, for the majority of the year do not meet P.W.Q.O. for ammonia,. and meet them only seasonally for pH.

Under low flows the Bud Creek zone of mixing extends approximately 300 metres downstream. Concentrations of dissolved substances are increased by the inputs from Bud Creek, compounding the existing degraded condition of the stream. Pollutant mass balances indicate that under low flow conditions, even without the influence an upstream effluent discharge, the Bud Creek source would result in river concentrations of ammonia and dissolved solids in excess of P.W.Q.O.

When the water quality of the upper Serpent River is evaluated in terms of P.W.Q.O., specifically Policy 5, the complete stretch of river downstream of Stollery Lake to Quirke Lake must be classified as a zone of non-compliance during certain seasons and flow conditions.

A natural waterfall just upstream of the Denison Mine access road defines the limit of fish migration on the upper Serpent River. Therefore, no definition of zone of passage need be considered at the Stollery Lake outfall.

Although a decline in numbers and diversity of benthic macroinvertebrates was noted below the effluent sources, the river's benthic community reflected only moderate alteration. The standing crop of benthic organisms is considered adequate should a re-introduction of fish be considered.

The results of the August, 1981, electrofishing survey support the hypothesis that, at least seasonally, the probability for fish survival under existing conditions is marginal.

Un-ionized ammonia has been identified as the principal toxicant of concern in the upper Serpent River system. Chemical analysis of the two effluents revealed ammonia levels that would be expected to be lethal. The degree of lethality to test fish of these effluents was found to be variable, with acute lethality occurring at effluent dilutions as low as 20% v/v. Experimental removal of ammonia eliminated the observed lethality, confirming un-ionized ammonia as the toxic component.

During the 1980 studies, un-ionized ammonia concentrations under low flow conditions were greater than P.W.Q.O. but below reported 96 hr.- LC_{50} values. Bioassay samples produced no adverse effects an zebra-Fish egg hatchability or fry survival.

Although the positive fish exposure results from 1981 are encouraging, the question of whether or not a re-introduced fishery would be sustained in the upper Serpent River remains undefined.

The concentrations of un-ionized ammonia in the river below the mixing zones are dependent on available dilution, ambient pH, temperature and ammonia loadings from the two effluent sources.

In particular, the toxicity of ammonia is very sensitive to pH. Ammonia establishes an equilibrium in water:

$$NH_3 + H^+ = NH_4^+$$

or $$\frac{[NH_3]\,[H^+]}{[NH_4^+]} = K = 10^{-4.3}$$ (Stumm and Morgan, 1970)

The un-ionized ammonia (NH_3] is the toxic chemical species. The higher the pH the greater the fraction of the total ammonia that is in the toxic un-ionized form. For example at a temperature of 20°C and pH = 6.0 only 0.040% of the total ammonia (NH_3 + NH_4^+) present will be toxic while at pH = 8 that fraction jumps to 28%, an increase of 700 times.

Un-ionized ammonia concentrations as high as 4.45 mg/L were documented in the river in 1981. This value is equivalent to that which caused complete fish mortality at the Stollery Lake Dam in two hours, during the May *in-situ* exposure.

Ultimately, milling processes with significantly lower ammonia losses need to be implemented. In the interim the observed toxicity could be reduced by maintaining the effluents at lower pH's (near neutrality). As there are potential harmful side effects of lower pH's in the effluent (greater losses of metals such as iron and lowered buffering ability necessary to offset the instream oxidation of ammonia) studies are required to ensure adequate protection of the receiving water.

Considering the seasonally variable toxicity of the river, there is the potential that a fisheries management strategy could be adopted that would exploit the period of favourable water quality, particularly if instream pH is lowered.

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APPENDIX A

EFFLUENT AND RIVER WATER QUALITY DATA

Appendix A Table A-1:
Water Chemistry Data Upper Serpent River - June 10, 1980.*

Station	Total NH_3-N	NO_3-N	Ca	Solids Sus.	Solids Diss.	Cond. (µmho/cm)	U (µg/L)	Cu	Zn	SO_4	pH
1	0.10	0.48	4	<5	28	43	<10	0.09	0.16	7	6.3
2	9.3	20.6	155	--	850	1100	48	0.06	0.29	---	---
3	14.0	32.9	230	<5	1308	1350	80	0.08	<0.05	610	7.8
4	14.0	33.4	235	--	1249	1600	83	0.06	0.07	---	--
5	16.4	37.4	265	<5	1475	1700	89	<0.02	<0.05	610	7.6
6	16.8	35.8	260	<5	1398	1650	90	<0.02	0.07	530	7.3
D-2	34.5	75.1	600	12	3502	3600	210	0.09	0.31	1500	8.4
Q-3	28.0	53.6	395	11	2037	2200	170	<0.02	0.20	1500	8.3

* All results in mg/L except as noted.

Appendix A, Table A-2

Bud Creek / Serpent River Mixing Zone Water Quality - June 10, 1980.

(mg/L except as indicated)

Station	Total NH_3-N	Nitrate	Calcium	Total Dissolved Solids	Conductivity (μmho/cm)	Uranium (μg/L)	Cu	Zn
4 *	14.0	33.4	235	1249	1600	93	0.06	0.07
P1	21.5	45.7	330	1831	1950	140	0.06	<0.05
P2	----	----	285	1489	1700	95	0.07	0.14
P3	16.4	37.3	265	1491	----	98	0.07	0.07
P4	17.7	41.1	275	1426	1650	97	0.08	0.14
P5	14.6	33.9	255	1437	1650	91	0.04	0.05
Q1	17.3	37.7	290	1580	1900	100	<0.02	<0.05
Q2	17.9	39.1	285	1594	1800	110	0.05	<0.05
Q3	17.6	38.6	290	1622	1800	100	0.06	0.06
Q4	17.7	39.1	230	1585	1750	100	0.06	0.12
Q5	16.2	36.8	265	1540	1700	89	0.05	0.05
R1	12.6	28.0	285	1502	1700	95	<0.02	0.07
R2	17.2	38.7	275	1527	1700	96	0.06	0.13
R3	16.7	37.2	275	1510	1700	96	<0.02	<0.05
R4	16.9	37.7	275	1394	1700	94	0.06	<0.05
5**	16.4	37.4	265	1475	1700	99	<0.02	<0.05

Note:

Transect P, O and R interval samples numbered beginning at North Bank.

* upstream boundary station

** station below mixing zone - shown for comparison

Appendix A, Table A-3

Chemical Characteristics of Mine Tailings Effluents before and after Treatment to Remove Ammonia.

Sample Name	Date	COD	Cond. μmho/cm @ 25°C	pH	Hard. as $CaCO_3$	Alk. as $CaCO_3$	Chemical Data mg/L NH_3-N	TKN	NO_2-N	NO_3-N	Ca	Mg	Na	K	Cl	SO_4	Sus. Solid	Diss. Solid
Stollery Lake Dam:																		
1. Untreated	June 10/80	39	3750	9.7	1620	43	43	43	8.0	118	640	6	152	130	202	1500	1	3230
2. Clinoptilolite Tr.	June 10/80	<20	4230	9.4	650	27	<0.1	0.60	6.0	89	255	3	755	2.6	202	1540	25	3270
Bud Lake Cr. Dam 'E':																		
1. Untreated	June 10/80	21	3125	8.5	1540	43	44	44	3.3	83	600	7	19	140	20	1500	11	2790
2. Clinoptilolite Tr.	June 10/80	<20	3450	8.5	783	33	<0.1	0.50	3.3	82	308	3	530	2.0	20	1520	40	2830

Sample Name	Date	Chemical Data mg/L Zn	Cu	Ni	Pt	Cd	Cr	Al	Mn	Fe	Ba	As	Co	Dias. Ra^{226}	Diss. U^{238}	Diss. Gr. α	Diss. Gr. β
Stollery Lake Dam:																	
1. Untreated	June 10/80	<.002	.020	.020	<.006	<.001	.008	0.64	0.140	0.28	0.360	0.006	0.010	1	130	180	110
2. Clinoptilolite Tr.	June 10/80	<.002	.009	.006	<.006	.001	.008	0.91	0.037	0.38	0.061	0.004	0.003	-	---	---	---
Bud Lake Cr. Dam 'E':																	
1. Untreated	June 10/80	.020	.020	.004	<.006	<.001	.007	1.1	0.230	0.86	0.44	0.004	0.01	1	110	150	98
2. Clinoptilolite Tr.	June 10/80	<.002	<.002	.004	<.006	<.001	.007	1.7	0.090	0.67	0.11	0.004	<.002	-	---	---	---

Appendix A, Table A-4

Chemical Characteristics of Mine Tailings Effluents and River Samples.

Sample Name	Date	COD	Cond. µmho/cm @ 25°C	pH	Hard. as $CaCO_3$	Alk. as $CaCO_3$	Chemical Data mg/L NH_3-N	TKN	NO_2-N	NO_2-N	Ca	Mg	Na	K	Cl	SO_4	Sus. Solid	Diss. Solid
Tailings Pond Effluents:																		
D-2	July 23/80	23	3970	8.8	1760	46	43	43	14	91	676	17	152	130	232	1600	<5	3480
Q-3	July 23/80	<20	3270	8.7	1660	43	43	13	5.3	95	651	9	20	150	21	1600	<5	2930
Serpent River Samples:																		
Stn.1 Dunlop Lake outlet		<20	36	7.5	13	7	0.2	1.0	0.01	0.1	5	<1	1	0.3	1	1	<5	38
Stn.3	July 23/80	<20	1295	7.6	482	14	11	11	1.3	26	189	2	41	33	64	450	<5	1290
Stn. 5	July 23/80	<20	1560	7.6	636	14	15	15	0.8	34	250	3	32	51	47	480	<5	1560

Sample Name	Date	Zn	Cu	Ni	Pb	Cd	Chemical Data mg/L Cr	Al	Mn	Fe	Ba	As	Co	Diss. Ra^{226}	Diss. U^{232}	Diss. Gr. α	Diss. Gr. β
Tailings Pond Effluents:																	
D-2	July 23/80	<.001	.001	.011	<.003	<.0002	<.002	0.44	0.097	.023	0.47	.020	.008	1	150	210	1200
Q-3	July 23/80	<.001	<.001	.0065	<.003	<.0002	<.002	1.2	0.13	0.29	0.24	.010	.006	2	55	92	1300
Serpent River Samples:																	
Stn.1	July 23/80	<.001	<.001	<.002	<.003	<.0002	<.002	.035	.0082	.034	.005	<.001	<.002	<1	<10	<1	----
Stn. 3	July 23/80	<.001	<.001	<.0032	<.003	<.0002	<.002	.081	.032	.018	.060	.004	<.002	2	32	57	440
Stn.5	July 23/80	.0017	<.001	.0062	<.003	<.0002	<.002	0.17	0.15	.087	.062	.003	<.002	2	72	60	520

Appendix F Table A-5

Chemical Characteristics of Mine Tailings Effluents from Mills Employing the NEAP and LAMIX Uranium Extraction Processes.

Sample Name	Date	COD	Cond. µmho/ cm @ 25°C	pH	Hard. as $CaCO_3$	Alk. As $CaCO_3$	Chemical Data mg/L NH_3-N	TKN	NO_2-N	NO_3-N	Ca	Mg	Na	K	Cl	SO_4
Tailings Effluents from NEAP [1] Mill Processes:																
Stollery Lake Dam D-2	Aug 20/90	<20	3750	10	1750	78	19.7	20	12	76	690	3	151	130	237	1460
Bud Lake Cr. Dam Q-3	Aug 20/80	<20	3200	9.3	1640	32	31.9	40	5.9	96	650	5	19	143	20	1500
Tailings Effluent from LAMIX[2] Mill Process:																
Panel Mill Outfall		20	2150	3.9	1220	20	3.4	5	0.39	4.1	470	12	28	51	48	1180

Sample Name		Chemical Data mg/L Zn	Ni	Pb	Cd	Cr	Al	Mn	Pe	Ba	As	Co
Stollery Lake Dam D-2	Aug 20/80	.001	.007	.008	<.005	.003	0.23	.009	.028	.25	.02	<.002
Bud Lake Cr. Dam Q-3	Aug 20/80	.003	.008	.010	<.005	.004	0.45	.074	.30	.17	.009	.003
Panel Mill Outfall		.020	.010	.020	<.005	.003	0.73	0.14	.24	.53	.002	.003

[1] NEAP - Nitrate elution and ammonia precipitation
[2] LAMIX - Limestone-Acid-Magnesia-Ion exchange

APPENDIX B

BIOLOGICAL DATA

APPENDIX B: TABLE B-1

Physical and Biological Characteristics of the Upper Serpent River

Station Number	Date	Streambed Characteristics	Estimated Rate of Flow (m^3/sec)	Substrate	Water Temp.	Air (°C)	Comments
1	21/07/80	50% EF/50% R	0.7	Cobble and Sand	23.5	24	Station below old control structure; poor bank and instream cover, no overhangs or undercuts; surrounding land use mixed forest and parking lot, fishy algal odour.
2	22/07/80	40% EF/20% R/40% P	1.4	Cobble over bedrock	22	26	Station below Stollery Lake; good spawning bed but limited bank and instream cover, surrounding land use forest.
3	22/07/80	100% R	1.4	Cobble over gravel and bedrock	23	24	Poor bank and instream cover, 80% cover of benthic algae, surrounding land use mixed forest.
6	22/07/80	100% R	2.8	Cobble	23	24	Station below Bud Lake, poor bank and instream cover, algal odour, surrounding land use forest.

EF - evenflow
R - riffle
P - pool

APPENDIX I: TABLE B-2
Numbers/m^2 and types of Macroinvertebrates
Collected from Four Stations in the Upper Serpent River - July, 1980.

(P indicates presence in qualitative sample.)

STATION:-	1					2					3					6				
Taxa	S-1	S-2	S-3	Qual	$\bar{x}$	S-1	S-2	S-3	Qual	$\bar{x}$	S-1	S-2	S-3	Qual	$\bar{x}$	S-1	S-2	S-3	Qual	$\bar{x}$
Stoneflies:																				
Acroneuria				P	P															
Paragnetina				P	P															
Mayflies:																				
Ephemerella		19			6															
Isonychia						19				6										
Caddisflies:																				
Cheumatopsyche	950	988	627	P	855	1159	228	57	P	481	1178	1425	380	P	994	361	247	342	P	317
Chimarra	57	76		P	44															
Hydropsyche			228	P	76	114	190	19	P	108	266	380	229	P	291	19	19	38	P	25
Limnephilidae														P	P					
Polycentropus														P	P					
Rhyacophilidae	57			P	19	209	285	95	P	196	304	95	114	P	171					
Pupae, unidentified case				P	P	19	19		P	13			38	P	13		19			6
Alderflies:																				
Chaliodes														P	P			19	P	6
Snails:																				
Planorbidae																			P	
Beetles:																				
Elmidae						380	1425	266	P	690	589	665	722	P	659			76		25
Haliplidae											19	19		P	13					
adults, unidentified									P	P				P	P					
Diptera:																				
Simuliidae	1691	779	1140	P	1203	1748	1843	1482	P	1691	380	57		P	146	19				6
Chironomidae		76	57		44	95	190	19		101	76	171	19	P	97	19	247	19		95
Flatworms	494	589	209		431	19				6										
Crayfish:																				
Cambarus				P	P															
Worms:																				
Lumbriculidae				P	P						19				6					
	S-1	S-2	S-3	Qual	$\bar{x}$	S-1	S-2	S-3	Qual	$\bar{x}$	S-1	S-2	S-3	Qual	$\bar{x}$	S-1	S-2	S-3	Qual	$\bar{x}$
Total Taxa	5	6	5	9	12	9	6	6	5	9	9	7	5	10	11	4	3	5	4	7
Total organisms/m^2	3249	2527	2261	-	2678	3762	4180	1938	-	3292	2831	2812	1501	-	2380	418	532	494	-	480
d, Margalef's Index	1.1	1.5	1.2		3.2	2.0	1.4	1.5		2.0	2.0	1.7	1.3		3.0	1.1	0.7	1.5		2.2

APPENDIX B: TABLE B-3
Numbers/ m^2 and types of Macroinvertebrates Collected from the Upper Serpent River — 1967 and 1968.

(Source: NE regional files and re-examination of original 1968 samples.)

LOCATION	1* 1967		6* 1967		1** 1968
	June	July	June	July	May
Caddisflies:					
Hydropsyche	38	342	19	437	703
Chimarra		19			
Polycentropus		19			
Cyrnellus				114	
Cheumatopsyche					57
Rhyacophila					19
Mayflies:					
Baetis		19			19
Heptagenia		19			
Pseudocloeon		19			
Stenonema	19				19
Stoneflies:					
Acroneuria		*19*			
Isoperla					38
Paragnetina					19
Beetles:					
Elmidae		19			
Crayfish:					
Cambarus bartoni		19			
Amphipoda:					
Hyallela azteca	38				
Worms:					
Lumbriculus variegatus		19			
True flies:					
Chironomidae	152	114	19	76	38
Simuliidae			1083	171	
Cnephia	380				
Flatworms					76
Total Taxa	5	11	3	4	9
Total organisms/m^2	487	524	1121	798	978
d, Margalef's Index	1.5	3.7	0.7	1.0	2.7

* - Surber sample only.
** - Surber plus qualitative sample.

APPENDIX C

IN-SITU CHEMICAL DATA

Appendix C: Table C-1

Serpent River Water Quality (May, 1981) at the Fish Exposure Sites

Chemical Data (mg/L) - 5-day averages.

Exposure Sites (Fig.6) No.	Cond. at 25°C µmho/cm	Hardness as $CaCO_3$	Alkalinity as $CaCO_3$	pH	NH_3-N*	TKN	NO_2	NO_2 + NO_3	Na	K	Cl	SO_4
F-1	33.6	9.6	11.8	6.8	0.036	0.21	0.002	0.0096	0.27	0.28	0.8	6.4
D-2	3495	1271	50	8.55	48	49.8	2.5	87.5	139.8	96.1	236	1254
F-3	331	90	11	6.85	1.97	2.7	0.6	5.4	23.4	3.3	9.9	84.4
F-4	184	55	3.3	6.4	2.21	3.7	0.6	5.2	12.1	3.6	25	104
Q-3	1536	535	22	7.3	32.5**	23	1.4	42	8.8	64	12.4	618
F-6	2300	837	26	7.35	46.1	48	2.1	65.3	12.5	102	15.8	981
F-7	690	212	14	6.4	8.5	9.6	1.5	15.2	13.0	21.2	21.9	213
F-8	614	184	14	6.85	7.9	9.5	0.7	12.1	11.5	17.9	22	186

* Based on estimated values in some cases - see Appendix III.

** Results at this station highly variable due to flow pattern shifts of effluent plume.

Chemical Data (mg/L) - 5-day averages or median values (*)

Exposure Sites (Figure 6) No.	Cu	Zn	Cd	Al	Pb	Ni	Cr	Fe	Ba	Ca
F-1	<.001*	.003*	.0003*	.024*	<.003*	<.002*	<.002*	.04	--	2.9
D-2	.018	.015*	.004*	.962	.003*	.009	.004*	.03	181	488
F-3	<.001*	.004*	<.0002	.071	<.003	<.002	<.002	.04	.062	33.7
F-4	<.001*	.003*	<.0002	.196	<.003*	<.002*	<.002	.03	.079	42
0-3	.006*	.022*	.0005*	.257	.003*	.010*	<.002*	.46	.124	203
F-6	.010	.013*	.0003*	.404	.003*	.012	.004*	.73	.172	318
F-7	<.004	<.006	<.0002*	.117	<.006	<.002	<.002	.10	.068	80
F-8	.003*	.009	.0006*	.101	<.003*	<.002*	<.002	.08	.100	69.4

* median values are cited in place of average values where raw data consists of values measured as being less than the detection levels.

Appendix C: Table C-2

Ammonia Levels (measured and/or calculated) for the 1981 *in-situ* Exposure Sites.

EXPOSURE SITES (see Figure 6) No.	NH_3-N VALUES ON TEST DAYS					Linear Equation ($y = NH_3$-N) (i.e. y = ammonia - nitrogen)	x = known values of	r value	n
	1	2	3	4	5				
F-1 (reference)	.038	.058	.034	.034	.016	all measured values	---	---	---
D-2	48.5	48.4*	46.0	48.5	49.1	N.A.	N.A.	N.A.	N.A.
F-3	1.87	1.79	4.45**	1.30	2.90	y = .4226x +.1794	$(NO_2 + NO_3)$-N	.975	4
F-4	1.50	1.65	5.20**	3.50	2.18	y = .8036x -.1430	Total Kjeldahl-N	.979	4
Q-3	46.6**	7.35**	68.5**	10.3	31.5	y = .7186x +.9576	$(NO_2 + NO_3)$-N	1.0	2
F-6	49.2**	49.7**	44.3**	43.0	49.2	y = .984x - 17.23	$(NO_2 + NO_3)$-N	1.0	2
F-7	6.04**	5.9	11.0	9.10	11.6**	y = 1.304x - 3.835	Total Kjeldahl	.968	3
F-8	8.25	7.0	6.85**	8.30	8.10	y= .4258x + 2.547	$(NO_2 + NO_3)$-N	.907	3

* Linear regression inappropriate - estimate based on NH_3-N/(NO_2-N + NO_3-N) ratio, which produced a value of 0.55 ± 0.02 [N = 3, $(NO_2 + NO_3)$-N value missing in fourth case].

** estimated values using linear regression analyses.

ADDENDUM

AMMONIA MONITORING AND TOXICITY TESTS
1983-84

1983-84 AMMONIA MONITORING AND TOXICITY TESTS

The results of fish bioassay studies performed in 1980-81 revealed that the final effluents from both the Denison and Rio Algom tailings areas were variably lethal to test organisms. However, toxicity tests conducted with caged fish held in the upper Serpent River, along with laboratory static bioassays, did not show lethal responses. High concentrations of ammonia and pH were identified as the factors controlling toxicity in the effluents.

The lack of lethal response for the river samples suggested that river conditions might be adequate to support fish. However, indications from water chemistry monitoring during 1981 showed that river concentrations of ammonia at times approached or exceeded. values that were known to produce fish mortality (Figure 4).

In 1983, an ammonia monitoring program was initiated to evaluate the seasonal patterns of ammonia distribution in the river. In addition, a toxicity testing procedure was undertaken for effluents and river stations four times during 1983-84.

Methods

Water chemistry samples were obtained from four locations on the upper Serpent River corresponding to stations F-1, F-3, F-4 and F-8 in Figure 6. The two tailings effluents, at Stollery Lake (D-2) and Bud Creek (F-6), were also sampled.

Temperature and pH were determined on-site while conductivity and alkalinity were analyzed in the Sudbury Regional laboratory. Ammonia was analyzed at the M.O.E. laboratory in London.

Water samples for toxicity testing were collected by Regional staff and shipped immediately to arrive within 48 hours at the M.O.E.

Toronto laboratory. Sampling dates were: August 28, 1983; December 1, 1983; February 14, 1984; and May 6, 1984. Additional water samples were collected on those dates and submitted for analysis of metals and characterization parameters.

Static laboratory fish toxicity tests of 96-hour duration were performed using rainbow trout to determine what effluent concentration would result in a 50% mortality of test fish (96-hour LC_{50}). River samples were tested in an undiluted state while a dilution series was prepared for the samples of effluent. In previous tests (1980), Toronto tap water was used as the diluent. In this series of tests, dilution water for the effluent samples was obtained from the sampling stations immediately upstream of the effluent outfalls. Results were expected to be more applicable to the actual field situation.

River flow data for stations F-1 and F-8 were obtained from Water Survey of Canada.

Results

Results of the toxicity tests are presented in Table A. Corresponding pH, total ammonia and calculated un-ionized ammonia concentrations (after Thurston, Russo and Emerson, 1979) are included. Acute lethality was indicated when test samples produced a 96-hour LC_{50} equal to or less than 100% concentration.

Station F-1, upstream of the effluent sources, was not lethal at any time.

At D-2 (Stollery Lake effluent), the August 23 and February 14 tests revealed acute lethality to test fish. The May 6, 1984,results were marginally lethal with 33% mortality in 100% effluent. No mortality was observed in the December 1, 1983, test. On this date, the concentration of total ammonia (57.0 mg/L) was comparable to that found in the lethal samples (48.5 mg/L to 106.0 mg/L) but the reduced pH (7.49) resulted in no deaths.

With the exception of F-3 in February, no mortalities occurred in the two river stations (F-3, F-4) immediately downstream of D-2. The February 14, F-4 sample caused 83% mortality of test fish in full strength solution. The total ammonia concentration was similar to the summer concentration, 32.75 mg/L versus 31.0 mg/L, but an elevated winter pH value (8.65) resulted in lethal responses.

At F-6 (Bud Creek effluent), acute lethality occurred in the winter samples, with 100% mortality in a <10% v/v sample. The effluent was extremely toxic. Sufficient dilution was not available to determine the LC_{50} concentration. The December 1, 1983, test was marginally lethal with 40% mortality in a full strength effluent solution. The calculated un-ionized ammonia concentration was 0.0092 mg/L, which is below the M.O.E. objective of 0.020 mg/L; however, the reported pH value (6.40) appears to be anomalous. The pH increased from F-4 (upstream of Bud Creek decant) to F-8 (downstream) while the reported effluent pH was lower. Based on a mass balance calculation of the H^+ ion concentrations, the expected pH for F-6 would be in the range of 7.8 to 8.8.

At F-8, only the February 14, 1984, sample resulted in acute lethality to test fish. The winter ammonia level was lower than the summer concentration (26.50 mg/L versus 36.00 mg/L), but the pH was elevated (8.8 versus 7.42), resulting in total mortality.

With the exception of the December 1983 and May 1984 samples, which were collected under high flow conditions, un-ionized ammonia concentrations in the river stations F-3, F-4 and F-8 exceeded the P.W.Q.O. of 0.02 mg/L (Table A). All effluent levels exceeded the objective, with the exception of F-6 on December 1, as discussed. In addition, the total ammonia effluent guideline of 10 mg/L was exceeded at both discharges (M.O.E. 1981).

The results of the 1983-84 ammonia monitoring program are presented in Table B. Calculated un-ionized ammonia concentrations in the river stations varied from <0.0005 mg/L to 0.4944 mg/L; and from <0.0005 mg/L to 8.7932 mg/L in the effluent samples. With the exception of periods of high flow (May, June and December), un-ionized ammonia concentrations in the river stations exceeded the P.W.Q.O. of 0.02 mg/L. Effluent concentrations of ammonia exceeded the 10 mg/L guideline on 12 of the 13 sampling dates.

As reported in Part III, the un-ionized ammonia LC_{50} for rainbow trout fingerlings ranged from 0.6 to 1.4 mg/L at the M.O.E. toxicity laboratory, but concentrations as low as 0.2 mg/L have been shown to cause fish mortality.

At D-2, 9 of 13 un-ionized ammonia determinations exceeded 0.6 mg/L. Effluent concentrations of un-ionized ammonia at F-6ranged from 0.0006 to 8.79 mg/L with 7 of the 13 determinations exceeding 0.6 mg/L.

Concentrations of un-ionized ammonia in the river stations downstream of the effluent discharges frequently exceeded 0.2 mg/L, but concentrations in excess of 0.6 mg/L were not detected. (Table B). The presence of un-ionized ammonia in the upper Serpent River in concentrations associated with fish mortality, indicates that adverse conditions to aquatic biota may frequently exist within the river.

Water chemistry results are presented in Table C. Individual copper, nickel, lead and zinc levels were below the guideline concentrations of 1 mg/L. Cumulative concentrations were also less than the respective guideline value.

At D-2 on August 23, the effluent guideline of 1 mg/L aluminum was exceeded. Elevated concentrations in the effluents were reflected in the downstream river stations.

All cadmium concentrations in effluents and river stations were below the P.W.Q.O.

Chromium concentrations at all river stations were below the objective. Effluent concentrations were within the Guidelines.

In conclusion, the results of the ammonia monitoring coupled with toxicity testing of effluents and river water support the conclusions reached in the 1980-81 studies. There is a distinct seasonal variability in the lethality of the two effluents.

In the winter months, due to ice cover, low reaction temperatures and slow oxidation of ammonia, the effluents were discharged to the river with elevated pH (>9.0) and ammonia. The low flows in the Serpent River (1.880 cm at F-8) provided reduced dilution. This combination of effects produced the lethal toxicity test responses observed in both effluents and river stations. For the remainder of the year, the pH of the effluents was lower (6.40 to 8.02). In combination with the higher flows in the spring and fall, all test samples were non-lethal. In summer when flows were lower than winter months (0.630 cm at F-8) but pH remained lower, no lethality occurred in the river stations.

Chemical monitoring shows concentrations of ammonia that continue to be periodically high in the river while pH and temperature conditions exist that enhance ammonia toxicity. The potential of ammonia toxicity to fish remains present in the upper Serpent River under the existing operating regime of the mining companies.

References

Ontario Ministry of the Environment, 1981. Guidelines for Environmental Control in the Ontario Mineral Industry.

Thurston, R. V., R. C. Russo and D. Emerson, 1979. Aqueous Ammonia Equilibrium-Tabulation of Percent Un-ionized Ammonia. E.P.A. - 600/3 -79-081.

JL/ml/REP40-H

TABLE A. Upper Serpent River - Results of 96-Hour Bioassays, 1983-84.

Station	Sampling Date	pH (lab)	Total NH_3 (mg/L)	Un-ionized NH_3 (mg/L)*	96-Hour LC_{50}	Mortality in Full Strength Solution	Flow Data (cm)
F-1 Dunlop	23/08/83	7.23	<0.005	<0.0005	non-lethal		0.041
Lake outlet	01/12/83	6.75	0.030	<0.0005	non-lethal		4.180
	14/02/84	6.54	0.030	<0.0005	non-lethal		1.520
	06/05/84	6.72	0.006	<0.0005	non-lethal		3.330
D-2 Stollery	23/08/83	8.02	48.500	1.3532	100%		
Lake decant	01/12/83	7.49	57.000	0.4782	non-lethal		
	14/02/84	9.08	106.000	26.2880	17%		
	06/05/84	7.94	88.600	2.0644	>100%	33%	
F-3 below	23/08/83	7.70	31.000	0.4185	non-lethal		
Stollery Lake	01/12/83	6.72	2.350	0.0034	non-lethal		
	14/02/84	8.65	32.750	3.5698	<100%	83%	
	06/05/84	6.88	7.400	0.0153	non-lethal		
F-4 above Bud	23/08/83	7.67	30.000	0.3780	non-lethal		
Creek	01/12/83	6.89	2.950	0.0063	non-lethal		
	14/02/84	7.96	22.750	0.5551	non-lethal		
	06/05/84	6.90	7.900	0.0171	non-lethal		
F-6 Bud Creek	23/08/83	7.75	37.400	0.5685	non-lethal		
decant	01/12/83	6.40	13.400	0.0092	>100%	40%	
	14/02/84	9.40	89.000	16.3760	<10%	100%	
	06/05/84	7.02	18.700	0.0535	non-lethal		
F-8 near Quirke	23/08/83	7.42	36.000	0.2574	non-lethal		0.630
Lake inlet	01/12/83	6.93	4.380	0.0102	non-lethal		4.320
	14/02/84	8.88	26.500	4.5580	<100%	100%	1.880
	06/05/84	6.87	8.600	0.0175	non-lethal		4.600

* tests conducted at 15°C

TABLE B. Upper Serpent River Calculated Un-Ionized Ammonia Concentrations 1983-84.

Station	Date	pH (field)	Temp. (°C)	NH_3 (mg/L)	Un-ionized NH_3 (mg/L)
F-1	25/05/83	6.83	10.5	0.005	<.0005
	08/06/83	6.69	12.0	0.210	<.0005
	30/06/83	6.78	20.0	0.005	<.0005
	14/07/83	6.98	24.5	0.005	<0.0005
	27/07/83	6.88	22.5	0.235	0.0008
	10/08/83	6.89	21.0	0.950	0.0031
	23/08/83	6.65	23.0	<.005	<0.0005
	13/09/83	7.06	17.5	0.005	<0.0005
	29/09/83	6.85	15.0	0.010	<0.0005
	20/10/83	6.84	10.5	<.005	<0.0005
	01/12/83	6.75	1.0	0.030	<0.0005
	14/02/84	6.20	1.0	0.030	<0.0005
	06/05/84	6.72	5.0	0.006	<0.0005
	06/06/84	6.95	12.0	<.002	<0.0005
D-2	25/05/83	-	-	-	-
	08/06/83	8.28	13.0	49	0.2102
	30/06/83	7.62	21.0	66	1.1550
	14/07/83	6.46	25.5	0.020	<0.0005
	27/07/83	7.83	23.0	52.0	1.6796
	10/08/83	8.01	22.0	42.5	1.9083
	23/08/83	7.75	21.5	48.5	1.1640
	13/09/83	7.52	19.0	63.0	0.7623
	29/09/83	8.34	14.0	56.0	2.9456
	20/10/83	8.21	8.0	49.0	1.2348
	01/12/83	7.49	1.0	57.0	0.1579
	14/02/84	8.45	2.0	106.00	2.8408
	06/05/84	7.94	5.0	88.60	0.9542
	06/06/84	7.48	14.5	61.20	0.4761
F-3	25/05/83	7.26	11.0	8.85	0.0500
	08/06/83	6.82	12.5	4.20	0.0063
	30/06/83	7.19	20.5	15.0	0.0951
	14/07/83	7.18	25.0	16.0	0.1397
	27/07/83	7.33	22.5	22.5	0.2266
	10/08/83	7.59	20.5	28.0	0.4424
	23/08/83	7.47	21.5	31.0	0.3937
	13/09/83	7.54	16.5	47.0	0.4944
	29/09/83	7.58	15.0	46.0	0.4738
	20/10/83	7.31	8.5	8.7	0.0293
	01/12/83	6.72	1.0	2.35	0.0011
	14/02/84	8.16	1.0	32.75	0.4192
	06/05/84	6.88	5.0	7.400	0.0070
	06/06/84	7.11	14.5	9.60	0.0321

Station	Date	pH (field)	Temp. (°C)	NH_3 (mg/L)	Un-ionized NH_3 (mg/L)
F-4	25/05/83	6.85	12.0	8.05	0.0200
	08/06/83	6.83	12.5	3.4	0.0052
	30/06/83	7.08	21.0	15.3	0.0782
	14/07/83	7.21	26.5	14.5	0.1472
	27/07/83	7.22	22.0	19.5	0.1474
	10/08/83	7.38	19.5	25.0	0.2275
	23/08/83	7.47	22.0	30.0	0.4020
	13/09/83	7.46	15.0	41.5	0.3249
	29/09/83	7.35	15.0	50.0	0.3045
	20/10/83	7.40	7.0	12.4	0.0456
	01/12/83	6.89	1.0	2.95	0.0021
	14/02/84	7.58	1.0	22.75	0.0776
	06/05/84	6.90	5.0	7.900	0.0078
	06/06/84	7.19	15.0	12.10	0.0511
F-6	25/05/83	5.18	12.5	16.25	0.0006
	08/06/83	8.92	12.0	6.9	1.0557
	30/06/83	8.28	19.5	43.0	2.9240
	14/07/83	7.72	27.5	37.0	1.2728
	27/07/83	7.84	21.0	47.0	1.3489
	10/08/83	6.96	19.5	-	-
	23/08/83	7.47	23.0	37.4	0.5386
	13/09/83	7.01	13.5	37.5	0.0934
	29/09/83	8.47	15.0	40.0	2.9920
	20/10/83	6.98	5.0	17.4	0.0207
	01/12/83	6.40	1.0	13.4	0.0030
	14/02/84	9.05	2.0	89.00	8.7932
	06/05/84	7.02	5.0	18.70	0.0245
	06/06/84	7.87	16.5	29.70	0.6623
F-8	25/05/83	6.64	12.5	13.5	0.0133
	08/06/83	7.19	12.5	6.3	0.0220
	30/06/83	7.32	21.0	21.0	0.1856
	14/07/83	7.37	26.5	17.6	0.2570
	27/07/83	7.18	21.5	23.5	0.1544
	10/08/83	7.17	19.0	24.5	0.1330
	23/08/83	7.18	24.0	36.0	0.2866
	13/09/83	7.49	14.0	32.5	0.2529
	29/09/83	7.47	15.0	38.0	0.3044
	20/10/83	7.34	6.5	18.5	0.0570
	01/12/83	6.93	1.0	4.38	0.0034
	14/02/84	8.31	0	26.50	0.4399
	06/05/84	6.87	5.0	8.60	0.0080
	06/06/84	7.24	16.5	13.10	0.0684

TABLE C. Upper Serpent River - Water Chemistry Results, 1983-84.*

Station No.	Sample Date	Cond.	Alk.	Al	Cd	Cr	Cu	Ni	Pb	Zn
F-1	23/08/83	32.2	7.2	0.021	<0.0002	0.002	0.005	<0.001	<0.003	0.002
	01/12/83	31.1	8.9	0.009	<0.0002	<0.001	0.002	<0.001	<0.003	0.003
	14/02/84	33.1	10.0	0.012	<0.0002	0.005	0.001	<0.001	<0.003	0.003
	06/05/84	32.1	6.6	-	-	-	-	-	-	-
D-2	23/08/83	3360.0	31.1	1.400	0.0007	0.009	0.037	0.071	0.006	0.024
	01/12/83	3180.0	26.3	0.140	<0.0002	0.001	0.012	0.018	<0.003	0.003
	14/02/84	3500.0	69.1	0.670	<0.0002	0.100	0.013	0.019	<0.003	0.005
	06/05/84	3580.0	29.2	-	-	-	-	-	-	-
F-3	23/08/83	2230.0	22.5	0.160	<0.0002	<0.001	0.021	0.005	<0.003	0.002
	01/12/83	225.0	9.0	0.030	0.0002	<0.001	0.002	0.003	<0.003	0.008
	14/02/84	1510.0	21.9	0.200	<0.0002	0.085	0.006	0.009	<0.003	0.004
	06/05/84	515.0	9.1	-	-	-	-	-	-	-
F-4	23/08/83	2210.0	20.6	0.160	<0.0003	<0.001	0.026	0.004	<0.004	<0.001
	01/12/83	268.0	9.7	0.030	0.0005	0.001	0.006	0.003	<0.003	0.005
	14/02/84	1249.0	22.8	0.140	<0.0002	0.069	0.006	0.007	<0.003	0.007
	06/05/84	524.0	9.6	-	-	-	-	-	-	-
F-6	23/08/83	2780.0	25.9	0.360	<0.0002	0.003	0.028	0.021	<0.003	0.008
	01/12/83	1056.0	3.5	0.420	<0.0002	<0.001	0.006	0.031	<0.003	0.018
	14/02/84	2440.0	91.9	0.280	<0.0002	0.027	0.010	0.008	<0.003	0.006
	06/05/84	1157.0	14.9	-	-	-	-	-	-	-
F-8	23/08/83	2090.0	18.7	0.210	<0.0002	0.002	0.027	0.015	<0.003	0.0012
	01/12/83	399.0	9.6	0.055	<0.0002	<0.001	0.007	0.003	<0.003	0.005
	14/02/84	1370.0	36.2	0.180	<0.0002	0.069	0.006	0.005	<0.003	0.006
	06/05/84	626.0	10.2	-	-	-	-	-	-	-

* All results in mg/L, except Cond. (μmho/cm at 25°C)