RRB 90-07

TOXIC EFFECTS OF INDUSTRIAL DISCHARGES ON WET LAND BIOLOGICAL COMMUNITIES

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January 1990
NWRI Contribution #90-53

ABSTRACT

Shock loading of toxic substances into waterways has substantial impact on the biota of natural water bodies. A threshold activated pump sampler was constructed to estimate the frequency of these shock loads in the study of two major industries that discharge their wastes into provincially significant (Class 1) wetlands. These shock loading events (sporadic discharges) occurred from 3 to 27 times per week during each of our 7 sampling intervals. Samples were taken during shock loading events from the receiving waters of a major chemical producer, (mean flow = 28,400 m^3 day^{-1}) using an RBR data logger and WS-10 pump sampler. These samples displayed elevated levels of a variety of compounds, especially toxic ammonia, calcium carbide, dicyandiamide, cyclo-octadiene, toluene, isobutylene and octene tri-ethyl pentyl phosphine. Acute toxicity (100% mortality) of caged emerald shiners (*Notropis atherinoides*), occurred following shock loading events associated with discharges from this company. The area in the Welland River downstream of this point source was bereft of all higher aquatic plants for a distance of approximately 70 m. Upstream of the company's outfall, the creek was colonized by dense stands of aquatic plants.

Samples removed from the Welland River, near the point source discharge of a major steel company (mean flow = 30,000 m^3 day^{-1}) had elevated levels of nickel, chromium, lead, zinc, copper, and iron during shock loading episodes. The area downstream of the steel company's discharge was occupied by a reef-like structure in which

nickel, chromium, lead, zinc and copper reached 3,550, 5,120, 760, 1050 and 610 mg kg^{-1} dry weight (ppm), respectively. This area was referred to as an "impact" or "dead" zone due to the complete absence of all higher aquatic plants from this portion of the provincially significant wetlands.

Key Words: Shock load impacts, sporadic toxic discharges, biological monitoring, riverine wetlands, macrophyte indicator assemblages, acute and chronic toxicity.

MANAGEMENT PERSPECTIVE

Toxic substance loading from industrial and municipal discharges into waterways has detrimental effects on the indigenous biota. Proper monitoring strategies for the detection of Sporadic toxicant discharge effects would help design effective regulatory programs.

This article describes the effective use of acute and chronic toxicity bioassays to detect the effects of industrial discharges containing electrolytes. The information presented in this report is of value to environmental researchers and managers in their environmental assessment programs.

INTRODUCTION

One of the most important tasks in the design of a regulatory water quality monitoring program is the selection of the appropriate sampling frequency given regulatory requirements (Casey et al., 1983). Sanders and Adrian (1978), for example, described a sampling strategy designed to detect individual violations of water quality standards by industries discharging toxic wastes on a sporadic basis. A method for optimizing the minimum time between samples which is required to detect sproadic industrial or municipal discharges was described by these same authors.

This paper describes a monitoring strategy for the detection of sporadic discharges which contain electrolytes. Modern data loggers designed to continuously monitor water quality using a variety of ion specific electrodes are ideal for this purpose. Because the sporadic discharges of most industries are usually associated with an increase in dissolved electrolytes, it is possible to detect shock loads by continuously monitoring changes in the specific conductivity of the receiving body at or near the discharge pipe.

Description of the Study Area

The Welland River is a shallow, slow-flowing, natural turbid clay-base river which flows along most of the length of the Niagara peninsula originating near Ancaster, Ontario and eventually emptying into the Niagara River (Fig. 1). At the Montrose Bridge near Chippawa, the river's flow is diverted into a canal (The Chippawa Power Canal) which empties into the Niagara River below the Sir Adam

Beck electric generating facility. The Welland River is used for a variety of industrial purposes as well as for recreational activities such as boating, swimming, water skiing and fishing.

One of the ecologically important aspects of the river is the large stands of aquatic macrophytes, primarily cattails and arrowheads, which line the river's banks. These macrophytes provide a habitat for numerous species of waterfowl, as well as other birds, muskrats, and fish (MNR 1984a). There is concern that the many stresses placed on the river are not only damaging its wetlands, but also constraining possible human uses such as the drinking water and recreation (Brady, 1985).

Wetland Ecology

Wetlands are among the most productive and the most threatened habitats worldwide (Euler, 1984). One of the two million hectares of presettlement wetlands found in Southern Ontario, over 80% have been severely altered or destroyed. Furthermore, losses in Southern Ontario of the remaining wetlands are presently occurring at a rate of one or two percent per year (MNR 1984a and b).

In Southern Ontario, many of the wetlands have been damaged or destroyed by rapid, unsustainable development. Anthropogenic stresses such as industrial and domestic pollutant discharges may damage these ecosystems. Two of the best remaining representatives of provincially significant riverine wetlands in the Niagara Peninsula are the class 1 (Provincially significant) Welland River and Lyons Creek wetlands (Ontario Ministry of Natural Resources, 1984a, 1984b, and Brady, 1985).

Shock Loading

Any discharge displaying a sudden pulse which affects the chemical or physical environment of a natural area for a brief period of time can be classified as a shock load (Von Tumling, 1969, Dickman, 1973). Waterways exposed to short term sporadic discharges (shock loads) from industries and municipalities are becoming a major focus of environmental concern.

The study of the impact of shock loading on a provincially significant (Class 1) wetland community in the lower Welland River was first undertaken in 1977 using two Lisle continuous conductivity recorders (Dickman et al., 1980 and Dickman et al., 1983). Later, this research was augmented by developing a threshold activated data logger connected to eight independently operated pump samplers. The data logger was designed to record temperature-corrected specific conductivity in the field while unattended for one to two weeks and to pump water from the receiving waters in 1 L nalgene bottles during shock loading events.

The Ontario Ministry of the Environment has been conducting a special survey, ("The Niagara River Improvement Team Survey" MOE, 1987) to examine the quantity and nature of the effluents being discharged into the Niagara River from all Canadian sources. The Welland River is the most important of these sources. The Niagara River Toxics Committee Report (1984) indicated that the Welland River was a source of heavy metal and nitrogenous contaminants for Lake Ontario. Two of the major discharges to the Welland River, according to this report, were the Cyanamid Canada (chemical) company and the Atlas Specialty Steels company. For this reason, our study focused on these two industries.

The Municipal Industrial Strategy for (pollution) Abatement in Ontario (MISA) is one of the few pieces of legislation in Canada which addresses the need for continuous monitoring in situations where sporadic sampling and average monthly concentrations prove to be inadequate because of the effects of shock loading.

METHODS

Monitoring included continuous conductivity, sediment sampling for heavy metals and benthic invertebrates. macrophyte distribution analyses as well as fish and cladoceran acute and chronic toxicity testing.

Sediment Sampling

Grab samples of sediment were taken from various points along the Welland River from 1986 to 1989 (Fig. 1). Samples were taken at industrial and municipal outfalls and at areas of particular interest such as the exposed reef-like structure adjacent to the outfall of the Atlas Steels plant (Fig. 2.).

Sediment grab samples were dried at 120° for 12 hr. The dried samples were passed through a 60 micron mesh nylon sieve and ground in a corundum mortar. A 2 g sample was treated with 20 mL of aqua regia, washed 3 times with distilled water, filtered (Whatman 541 filters) and made up to 100 mL with deionized water.

Filtered water samples from Atlas Steels were analyzed for Cu, Fe, Cr, Ni, Pb, and Zn using a D.C. Plasma Atomic Emission Spectrometer, AAS and ICP standard analysis techniques. Those taken from Cyanamid Canada were anlayzed for nitrogenous compounds using standard analysis techniques. (American Public Health Association 1975). Standards were prepared from primary standard reagents or from 99.99% pure elements.

Benthic invertebrates, primarily chironomids, sludge worms (aquatic oligochaetes) and molluscs, were sorted from sieved (0.47 mm mesh) Ekman dredged sediment samples. The sorted invertebrates were identified and preserved in buffered formalin. Only the chironomid data are reported here.

Continuous Conductivity Monitoring

A continuous recording Model S1-1 Lisle Specific Conductivity meter was installed at a location on the Welland River upstream of the confluence of Thompson's Creek (Fig. 1, Site E) and an RBR data logger was placed in the Cyanamid discharge which enters Thompson's Creek. The 2 meters were intercalibrated at daily intervals using a freshly calibrated YSI specific conductivity meter.

For studies of the Atlas-Mansfield storm sewer, which receives the Atlas Steels' effluent, the Lisle meter was installed upstream of the storm sewer, the RBR data logger (Fig. 3) was installed with it conductivity probe located inside the Atlas-Mansfield storm sewer and a third continuous conductivity meter was installed (with the permission of the company) inside the confines of the Atlas Steel Plant. Peaks in specific conductivity below either of the two outfalls which did not occur upstream were assumed to result from "shock loading" events.

Threshold Activated Pump Sampler

A model WS-10 water sampler (Brancker, 1987) was desinged to take sequential fixed volume (800 mL) samples. The unit was triggered by an external pulse and designed specifically for use with a RBR data logger (Model XL200L; Brancker, 1987). Water samples from upstream of the two aforementioned industries rarely exceeded 400 microSiemens/cm. Whenever the conductivity downstream of the receiving waterbody remained below a threshold of 400 µS cm^{-1} for 30 minutes, (a reading was taken every minute) and then rose above this threshold for 1 reading interval (1 minute) the RBR 8-channel data logger signalled the pump sampler of a shock loading event. As a result, the pump sampler withdrew an 800 ml sample from the receiving water body and stored it in a Nalgene bottle until we could remove it and transport it back to the laboratory for analysis.

The pump sampler intake flow rate was approximately 1 litre/minute. The pump sampler measured 5 x 15 x 15 cm (weight = 0.8 Kg) and employed a 12 volt DC marine battery which was recharged using a standard car battery charger. The diameter and length of the RBR data logger (Fig. 3) was 6 cm and 43 cm respectively (weight = 1.3 kg).

Each data logger entry used 2 bytes per channel and a 6 bytes time code was stored in the logger once a day and after each shock load. Storage of the data was performed by an 8 bit CMOS microprocessor using 4 alkaline AA internal batteries. Details of operation of the RBR data logger and pump sampler are available from Richard Brancker Research Limited, 27 Monk Street, Ottawa, Ontario K1S 3Y7.

Macrophyte Survey

The rooted aquatic plants were divided into four general categories based on the percentage of their above ground tissue which is in contact with the water:

1) long stemmed higher aquatics (e.g. cattails and bullrushes) have from 0 to 30% of their above ground biomass underwater.
2) the short stemmed aquatics such as the arrowheads and burr weeds typically have 20-60% of their above ground biomass underwater:
3) Floating leaved aquatics such as the water lilies and some of the pondweeds have between 40 and 80% of their biomass under the surface of the water and
4) The submersed aquatics, as their name implies, grow below the water's surface. These distinctions are not trivial when it comes to evaluating the impact of a water-borne toxin on the aquatic plant community. In general, the greater the surface area of the plant surface exposed to the water the more susceptible the plant is to water borne toxins.

To assess aquatic plant distributions, a 0.2 km distance above and a 2 km distance below each of the two point sources, on the Welland River was walked and the species composition and relative abundance of each taxon was noted. The aquatic plant zonation pattern above and below each of the point sources was then mapped.

Emerald Shiner Toxicity Tests

Fish holding cages measuring 25 cm long x 16 cm high x 16 cm wide were constructed using nontoxic plastic mesh and garden binder twine. Four adult emerald shiners (Notropis atherinoides) were placed in each net. Two cages were placed in the receiving water body downstream of the point source, and two were placed upstream as "controls". The conductivity, temperature and pH were recorded at each location. A Lisle Conductivity meter and/or RBR Data Logger remained on site for the 96 hour duration of the fish toxicity experiments.

Cladorceran Toxicity Tests

The standard 7 day cladoceran chronic toxicity test using Ceriodaphnia reticulate (Mount and Norberg 1984) was performed using samples which we collected following shock loading episodes at Cyanamid and Atlas Steels. In addition, a 48 hour bioassay was carried out by introducing ten D. magna which surviving was determined after 1, 2, 4, 8, 16, 24, and 48 hours. The EC_{50} was calculated after 48 hours according to the protocol for determining the acute lethality of liquid effluents (MOE 1983).

Benthic Invertebrates

A standard 15.3 x 15.3 cm Ekman Dredge was used to remove the sediment samples from the Welland River. The Ekman penetrated the mud and clay sediments found in the Welland River to a depth of approximately 4 cm. To collect enough chironomid larvae for statistical analysis, at least 3 replicate Ekman samples were collected from each site. Where chironomids were scarce, up to 62 Ekman samples were collected in an effort to gather a minimum of 30 individuals per site.

The dredged sediments were transferred to a bucket equipped with a 0.75 mm mesh sieve at its base. Each sieved sample was placed in a container and labelled by location number. The sorting was completed within 24 hours of the sampling date for all unrefrigerated samples and with a three day period of refrigerated samples.

Sorting

Once in the lab, each sample was placed again in a sieve with a 0.75 mm mesh and thoroughly rinsed with tap water. The resieved sample was then spread out in a large tray and covered with about 1 cm of tap water so that the life forms could be easily observed and separated. The specimens were removed with forceps and place in a 7% formalin solution (Pimental, 1967). Two coded vials were used: one for chironmids and one for other invertebrates. All the specimens were sorted out but only the chironomids were identified to the generic or species level. Chironomids were identified with the help of Mr. Bill Morten of Guelph, Ontario, using taxonomic keys by Oliver and Roussel, 19832 and Wiederholm, 1983.

RESULTS AND DISCUSSION

Biological Toxicity Tests

The acute toxicity of the Atlas Steels storm sewer shock load discharges to the Welland River was estimated from caged fish (Emerald shiners) which were placed immediately downstream of the Atlas Steels discharge point source, the Atlas-Mansfield storm sewer (Fig. 2). the Emerald shiner mortality was negligible over the 96 hr. exposure period suggesting that acute toxicity was not a problem. In addition, chronic toxicity tests were carried out using Ceriodaphnia-reticulata. The Ceriodaphnia-reticulata EC_{50} for this effluent was 30%. From these tests it was concluded that Atlas Steels' shock loads display a low level of chronic toxicity as indicated by the Ceriodaphnia-reticulata responses. Other studies of heavy metal toxicity frequently failed to display any acute toxicity but did register significant chronic toxicity responses (Koeman and Strik, 1975).

Sediment samples from the Welland River downstream of Atlas-Mansfield storm drain had exceptionally high levels of heavy metals (Table 2 and Fig. 4). No invertebrates were observed in the Ekman samples taken within a 10 m radius of the discharge pipe. Only sludge worms, primarily Liumnodrillus hoffmeisteri, colonized the area from 10 to 30 m downstream from the Atlas Steels outfall. Chironomids, crustaceans and clams which were common at upstream sites (Fig. 1, Site A) were rare in zones 1 and 2 below the Atlas discharge pipe (Fig. 4).

Cyanamid Monitoring Results

Shock loading events observed near the mouth of Thompson's Creek were frequently associated with the discharge of nitrogenous wastes. In 1984, Cyanamid Canada (an industrial chemical and fertilizer producer) discharged 28,400 m^3 day^{-1} of waste water containing a variety of nitrogenous compounds into Thompson's Creek (MOE, 1987). On some previous occasions when shock loads occurred (e.g. in 1979) the entire creek turned a vivid yellow-orange colour (Fig. 5). In general, however, the Cyanamid effluent was colourless and a sharp conductivity "spike" resulted when nitrogenouscompounds were released into Thompson's Creek (Figs. 6 & 7). These shock loads were acutely toxic (EC_{50} = 0.1%) based on standard Daphnia magna acute toxicity tests.

Cyanamid Sporadic Discharges

Fish placed in plastic mesh cages located in the Welland River and in Thompson's Creek near it confluence with the Welland River were monitored over a 96 hour period. During periods when no shock loading occurred, the fish survived for the 96 hour exposure period. Following shock loading events, however, a 100% mortality of the fish in the cages was observed with 24 hours of a shock loading event (Figs. 6 & 7). Mortalities of emerald shiners in the 2 upstream (control) cages never exceeded 12% (i.e. 1 fish out of 8, Figs. 6 & 7). On average, roughly 10 shock loads (specific conductivity greater than 2.0 times background) were observed each week during the 1987 Oct.-Nov. 8 week monitoring period. During this period, specific conductivity in the Welland River upstream of Thompson's Creek remained fairly constant (200-250 $\mu S\ cm^{-1}$).

None of the 27 Ekman samples taken from Thompson's Creek (1987-1989) 200 m downstream of the Cyanamid discharge had any chironomids. One or more of the chemicals discharged at this site (i.e., those listed in the Niagara River Toxics Committee Report 1989) and calcium carbide, dicyandiamide, cyclo-octadiene, toluene, isobutylene and octene tri-ethyl pentyl phosphine may have been responsible for the absence of chironomids (Sax, 1984).

Because we could not find any chironomids near the Cyanamid discharge site and because 100% mortality of caged fish occurred after each Thompson's Creek shock loading event, we concluded that the Cyanamid effluent being discharged into the Welland River via Thompson's Creek was toxic during shock loading episodes. Furthermore, we suspected from this and previous research (Dickman et al., 1980, Dickman & Steele 1986) that toxic discharges were the reason for the impoverished benthic invertebrate community and the complete absence of all higher aquatic plants downstream of the Cyanamid discharge (Fig. 8).

Floristic Zonation Pattern

Those plants with the largest exposed surface areas are typically the most sensitive to water-borne toxins (Dickman et al., 1983). Thus, all else being equal, the larger the percentage of exposed surface are, the more sensitive the plant to dissolved pollutants. this macrophyte differential sensitivity was indicated by a longitudinal zonation pattern in which the least sensitive (most tolerant) plant (typically the long stemmed aquatics) were found nearest the toxic point source (Fig. 4 & 8) while the least tolerant forms (e.g. the submersed taxa such as the water milfoils and the Canada water weeds) were located furthest form the toxic point source. This zonation pattern provides water managers with a useful index for evaluating the relative toxicity of a point source discharge (Pittwell 1986).

The distribution of higher aquatic plants below industrial outfalls (Figs. 4 & 8) was used to characterize their spatial zonation pattern. An impact zone (indicated by an area free of aquatic vegetation) occurred immediately below Atlas steels (Fig. 4, zone 1) and at Cyanamid Canada's Thompson's Creek and at the confluence of Thompsons Creek and the Welland River for a distance of 70 m (Fig. 8, Zone 1). Three contiguous recovery zones were identified (Figs. 4 & 8). Zone 2, the primary recovery zone, was characterized by tall emergent higher aquatic plants (e.g. macrophytessuch as cattails (Typha), sedges (Carex) and bullrushes (Phragmites). Zone 3, the secondary recovery zone, was characterized by short stemmed emergent macrophtyes (e.g. pickerelweed (Pontederia), arrowhead (Sagittaria) and burweed (Sparganium) as well as floating leaved macrophytes (e.g. water lilies (Nuphar and Nymphea). Zone 4, the tertiary recovery zone, was characterized by the presence, for the first time, of submersed macrophytes (e.g. Canada waterweed (Elodea), coontail (Ceratophyllum) and water milfoil (Myriophyllum).

Inorganic Analysis

In the initial work on the Welland River, shock loads of electrolytes and associated non-electrolytes were observed at the Atlas Steels outfall (Fig. 2, the Atlas-Mansfield storm sewer). On these occasions of the entire area around the discharge pipe would turn a bright reddish orange colour. These shock loads with their associated increases in conductivity (Fig. 9) were due largely to the elevation of calcium, carbonates and iron oxides. During these shock load events, calcium carbonate levels rose from a background concentration of around 75 ppm to over 300 ppm and iron oxide levels rose from a background of 5 ppm to over 250 ppm. Most of the iron was readily identifiable as hydrated iron oxide. On the basis of determinations made to date near the Atlas Steels outfall, it is evident that substantial quantities of heavy metals have accumulated in the downstream sediments of the Welland River (Table 2 & Fig. 4).

The levels of heavy metals in the sediments adjacent to the Atlas-Mansfield storm sewer were well above background (Thornton, 1983. Table 1) and were similar to those found in the reef-like structure which is located near the Atlas-Mansfield storm sewer (Fig. 2). A comparison of the data from the two control sites (Lyons Creek, Fig. 1 Site F) and the upper Welland River (Fig. 1 Sites A and B, & Table 1) indicated that the two areas were rather similar with respect to their sediment heavy metal concentrations. This observation was consistent with the history of the control sites which has been essentially agricultural. The concentrations of the various elements analyzed at these 2 agricultural sites lie within the normal range of these elements in soils (Table 1) and given by Thornton (1983). The sediment concentrations of heavy metals at the Atlas-Mansfield storm sewer, often exceeded the maxima described by Thornton (Table 1). Similar results were reported by Dalrymple and King (1985).

During shock loading events, a highly flocculent red coloured iron oxide (Fig. 2) was often discharged into the Welland river from the Atlas-Mansfield storm sewer. During severe episodes of shock loading, the Welland River itself would turn a bright reddish orange (Fig. 2). The ironoxide floc which Atlas discharged behaved as a sequestering agent accumulating lead, chromium, nickel and other heavy metals (Table 2). Analysis of the sediments near the Atlas outfall revealed significant increases above background of Ni, Cr, Pb, Zn, Cu and Co (Tables 1 & 2). Much of the iron oxide released during shock loading events settled out in the "dead zone" around the outfall. A reef-like structure (Fig. 2) was the result. As previously noted, the reef-like structure was barren of all higher aquatic plants.

SUMMARY AND CONCLUSIONS

The relationship between the biotic zonation pattern below an industrial outfall and the toxicity of that industry's discharge is complicated by the fact that few industries discharge their toxic wastes in a continuous fashion. Shock loading is the rule rather than the exception (Dickman, 1975). An "impact zone" in which all higher aquatic plants were absent extended approximately 2 km in length in Thompson's Creek below the Cyanamid discharge point source. This "dead zone" (zone 1) extended into the Welland River to include a 70 m long strip of a provincially significant Wetlands (Fig. 8).

The first higher aquatic plant (Phragmites communis), which we encountered downstream of the Atlas Steels discharge was located approximately 20 m below the Atlas-Mansfield storm sewer outfall.

Aquatic plants and their associated aquatic biota (e.g. benthic invertebrates (respond to peak loads and peak discharge toxicity levels rather than mean levels. Thus, if our goal is to protect the natural biota of our waterways, the calculation and reporting of each industry's annual and monthly discharge averages must be supplemented with peak loads and peak concentrations.

Emerald shiners (Notrophis atherinoides) placed in plastic mesh cages anchored to the riverbed below the Cyanamid discharge point source exhibited a 100% mortality following shock loading events in Thompson's Creek. However, acute mortalities (96 hour LD_{50}) did not occur in the absence of shock loading events. At the Atlas-Mansfield site, frequent sporadic discharges of iron oxides containing high concentrations of heavy metals resulted in acute toxicity of Daphnia magna (EC_{50} = 30%).

In conclusion, it would appear that if the natural biota of our waterways are to be protected, we must assign discharge concentration limits based on allowable maxima. Monthly and annual mean concentrations are meaningless when it comes to the calculating exposure times as related to the differential survival of the aquatic biota. As a result, continuous monitoring and the use of natural instream biological monitors should replace sporadic spot samples and composite sampling in all water quality programs which have as their primary goal the protection of the natural biota of our lakes and rivers. Where point source discharges contain electrolytes, continuous specific conductivity monitoring permits a better estimate of the frequency and intensity f shock loading events than does composite sampling.

ACKNOWLEDGEMENTS

The work outlined in this paper was supported by grants from the Wildlife Toxicology Fund, Environment Canada, the Ontario Ministry f the Environment, The Ontario Ministry of Employment and Immigration, and the Canadian Department of Fisheries and Oceans. Inorganic analyses were performed at Brock University by Mary Hanrahan, Anne Wei Chu, Margaret Best, and Pancy Tam. The fish acute toxicity tests were carried out by Robb Irvine.

We are especially grateful to Dr. Frank Johnson of Richard Brancker Research Limited, 27 Monk Street, Ottawa, Ontario K1S 3Y7 for designing the RBR recorder and to Dr. John Middleton of Brock University for his helpful comments on wetland areas.

REFERENCES

American Public Health Association, Standard Methods for the Examination of water and wastewater. 14th Edition. 1193 pp. (1975).

Brady, R.F., Natural areas of the Niagara Region: a preliminary survey. Planning and Development Department, Regional Municipality of Niagara, Thorold, Ontario, Ontario (1985).

Brancker, R., The RBR Data Logger (Model XD200L). Richard Brancker Research Ltd., 27 Monk Street, Ottawa, Ontario K1S 3Y7 (1987).

Casey, D., P.M.Nemetz, & D.H. Uyeno. Sampling frequency for water qualitymonitoring: measure of effectiveness. Water Resources Research 19: 1107-1110 (1983).

Dalrymple, R..J. and L.W. King. Canadian Point Sources to the Niagara River. Final report on M.O.e. and E.P.s. 1981/82 surveys. NRTC Appendix report, Toronto, Ontario, 157 pp. (1985).

Dickman, M. Total dissolved electrolyte effects on periphyton. J. Water Pollution Control Federation 45: 2211-2215 (1973).

Dickman, M. A comparison between the effects of sporadic and continuous loading from sulphite paper mills on attached algae in the Ottawa River near Ottawa, Canada. Proc. Water Pollution Research 10: 65-72 (1975).

Dickman, M., J. Smol and Steele. The impact of industrial shock loading on selected biocoenoses in the lower Welland River, Ontario. Water Pollution Research Journal of Canada 15: 17-31 (1980).

Dickman, M., Prescott and K.L.E. Kaiser. Variations in the aquatic vegetation in the Welland River (Ontario, Canada) above and below an industrial waste discharge. J. Great Lakes Research 9: 317-325 (1983).

Dickman, M., and Steele. Gonadal neoplasms in wild carp-goldfish hybrids from the Welland River and near Niagara Falls, Canada. Hydrobiologia 134: 257-263. (1986).

Euler, D.L. and others. An evaluation system for wetlands of Ontario south of the precambrian shield. Second edition Ontario Ministry of Natural Resources, Whitney Block, Queen's Park, Toronto, Ontario (1984).

Kaiser, K., M. Comba and H. Hunealt. Volatile halocarbon contaminants in the Niagara River and in Lake Ontario. J. Great Lakes Research 9: 212-223 (1983).

Koeman, J.H. and J.J.T.W.A. Strik. Sublethal effects of toxic chemicals on aquatic animals. Elsevier, Amsterdam. 234 pp. (1975).

Lan, Q., M.D. Dickman and B. Barclay. Genotoxicity studies of sediment samples from the Welland River, Regional Niagara, Ontario. Ontario Ethology and Ecology Conference. April 17-19, 1988. University of Western Ontario, London, Ontario N6A 5B7 (1988).

Ministry of the Environment. (MOE) Protocol to determine the acute lethality of liquid effluents to fish. MOE Toxicity Unit, Quality Protection Section, Water Resources Branch, Resources Rd., Rexdale, Ontario M9W 5L1 (1983).

Ministry of the Environment. (MOE) Priority chemical loadings from Ontario point sources discharging to the Niagara River. 1981-1987. ISBN 0-7729-2981-5. River Improvement Project Update Report. M.O.E. Hamilton, Ontario (1987).

Mount, D.I. and T.J. Norberg. A seven-day life cycle Cladoceran toxicity test. Environmental Toxicology and Chemistry 3: 425-434 (1984).

Niagara River Toxics Committee Report. U.S. Environmental Protection Agency New York, N.Y. Ontario Ministry of the Environment, Toronto, Ontario; Environment Canada, Toronto, Ontario; New York State Dept. of Environmental Conservation, Albany, N.Y. p. A-26 (1984).

Oliver, D.R. and M.E. Roussell. Insects and arachnids of Canada. Part 11. Genera of larval midges of Canada. Agriculture Canada Publication no. 1746. 263 pp. (1983).

Ontario Ministry of the Environment. (M.O.E.) Update Report on the Priority Chemical Loadings from Ontario Point Sources Discharging to the Niagara River (1981-1987). Toronto, Ontario. Queen's Printer, ISBN 0-7729-2981-5. (1987).

Ontario Ministry of Natural Resources. (MNR) An evaluation system for wetlands of southern Ontario south of the precambrian shield; second edition. Toronto Ontario Ministry of Natural Resources (1984a).

Ontario Ministry of Natural Resources. (MNR). Guidelines for wetlands management in Ontario. Toronto, Ontario Ministry of Natural Resources (1984b).

Pimentel, R.A. Invertebrate Identification Manual. Reinhold Publishing Corporation, New York-Amersterdam-London (1967).

Pittwell, L.R. Methods for the use of aquatic macrophytes for assessing water quality 1985-86. In Methods for the Examination of Waters and Associated Materials. Available from Her Majesty's Stationary Office or from The Secretary, The Standing committee of Analysts. Department of the Environment, Romney House, 43 Marsham Street, London, SW1P 3PY, England. (1986).

Sanders, T.G. and D.D. Adrian. Sampling frequency for river quality monitoring. Water Resour. Res. 14: 569-576 (1978).

Sax, N.I. Dangerous Properties of Industrial Materials (6th edition). Van Norstrand Reinhold Co. Inc., N.Y. and Toronto, 3124 pp. (1984).

Thornton, Iain. Geochemistry applied to agriculture. In Thornton, Iain (editor), Applied Environmental Geochemistry, Academic Press, New York, N.Y., p. 235 (1983).

Von Tumling, W. Suggested classification of water quality based on biological characteristics. Fourth International Water Pollution Research Conference. Pergamon Press. 4: 40-42 (1969).

Table Caption

TABLE 1. Sediment Concentrations (mg g^{-1} dry wt) of metals in the sediments of the Welland River near Atlas Steels and at control sites located upstream (Upper Welland River) and downstream (Lyon's Creek). For purposes of comparison, average sediment concentrations of Ni, Cr, Pb, Zn, Cu, and Co are provided under the column headed "Thornton" (1983).

The two columns near the right hand margin under the heading "WATER" represent MOE data for the metal concentrations (mg l^{-1} as annual means) in the Atlas Steels discharge to the Welland River for 1985 and 1986 respectively.

TABLE 2. Concentrations of Cr, Pb, Fe, Ni, Zn and Cu, (mg g^{-1} dry wt) in the sediments of the Welland river near Atlas Steels. Numbers refer to locations noted in Figure 3.

FIGURE CAPTIONS

1. Location map of Welland river study sites (A and B = upstream controls, C and E = Atlas and Cyanamid respectively, F = Lyon's Creek Control site) with inset of study area between Lakes Erie and Ontario.
2. Example of shock loading episode of heavy metals and iron oxides entering the Welland River from the Atlas-Mansfield Storm Sewer. The heavy metal contaminated "reef" jutting up above the water's surface in the background is located immediately in front of the Atlas-Mansfield storm sewer (visible as horizontal line in background).

3. The RBR XL200L Data Logger and WSD-10 Water Sampler.

Details of operation are provided in the methods section of the text.

4. Observed concentrations of Cr, Pb, Fe, Ni, Zn, and Cu, (mg g^{-1} dry wt) in the sediments of the Welland river near Atlas Steels indicated by the numbers in the river which refer to entries in Table 2. Numbers on shoreline refer to the higher aquatic plant zonation pattern in the Welland river immediately above and below the Atlas-Mansfield storm sewer discharge.

5. Photographic evidence of Cyanamid shock loading in 1979 during an unreported discharge to Thompson's Creek.

6. Continuous specific conductivity profiles from above and below the confluence of Thompson's Creek and the Welland River for October 1987. Results of the 96 hour caged fish mortality study are depicted at the top of figure 7 and 8.

7. Continuous specific conductivity profiles from above and below the confluence of Thompson's Creek and the Welland River for October 1987. Results of the 96 hour caged fish mortality study are depicted at the top of figures 7A & 7B. The RBR data logger.

8. A schematic representation of the floristic zonation pattern downstream of Cyanamid and Thompson's Creek. Zone 1 (0-70m downstream of the confluence of Thompson's Creek) as denoted as 1. Zone 2 (70-100 m downstream of the confluence of Thompson's Creek) was denoted as "2a" by a small stand of rushes. Zone 3 (100-400 m downstream of the confluence of Thompson's Creek) was denoted as "3a" by a small stand of pickerelweed (short stemmed emergents). Zone 4 extended to the Montrose Bridge where the waters of the Welland river are diverted into the rock-lined "Chippawa" Power Canal. Submersed aquatic plants were plentiful upstream of Thompson's Creek (Zone 5).

9. A typical one week period (18-24 Nov. 1987) using the RBR data logger temperature corrected conductivity below the Atlas Steels' point source as evidence of "shock loading".

TABLE 1

Sediment Concentrations of Heavy Metals in the Welland River Watershed[1]

Parameter Tested	SEDIMENT: Upstream of Source			SEDIMENT: Downstream of Source			WATER	
	Upper Welland	Lyons Creek	Thornton 1983	Atlas Steels Sediments	Atlas Steels Reef[2]	Atlas Steels Shock load	MOE[3] 1985	MOE[3] 1986
							mg/l	mg/l
Nickel	29.5	44.9	2-100	3927 ± 600	2900	3800	.0233	0.115
Chromium	30.0	33.7	N.A.[4]	3712 ± 130	2100	3640	.0067	0.129
Lead	68.0	72	10-150	800 ± 200	2210	950	.500	n.d.[5]
Zinc	127	111	25-200	1088 ± 100	n.d.[5]	720	.0833	0.144
Copper	27.6	28.6	2-60	753 ± 77	2450	815	.0267	.0456
Cobalt	N.A.[4]	N.A.[4]	N.A.[4]	237 ± 43	300	220	N.A.[4]	N.A.[4]

1 mg/g dry weight (except as noted)

mean of 3 samples

3 MOE 1987 Report (see references). Values represent annual means based on monthly samples.
1985 levels in the water are based on an estimated discharge of 29,000 m^3/day
1986 levels in the discharge water are based on an estimated mean discharge volume of 28,400 m^3/day

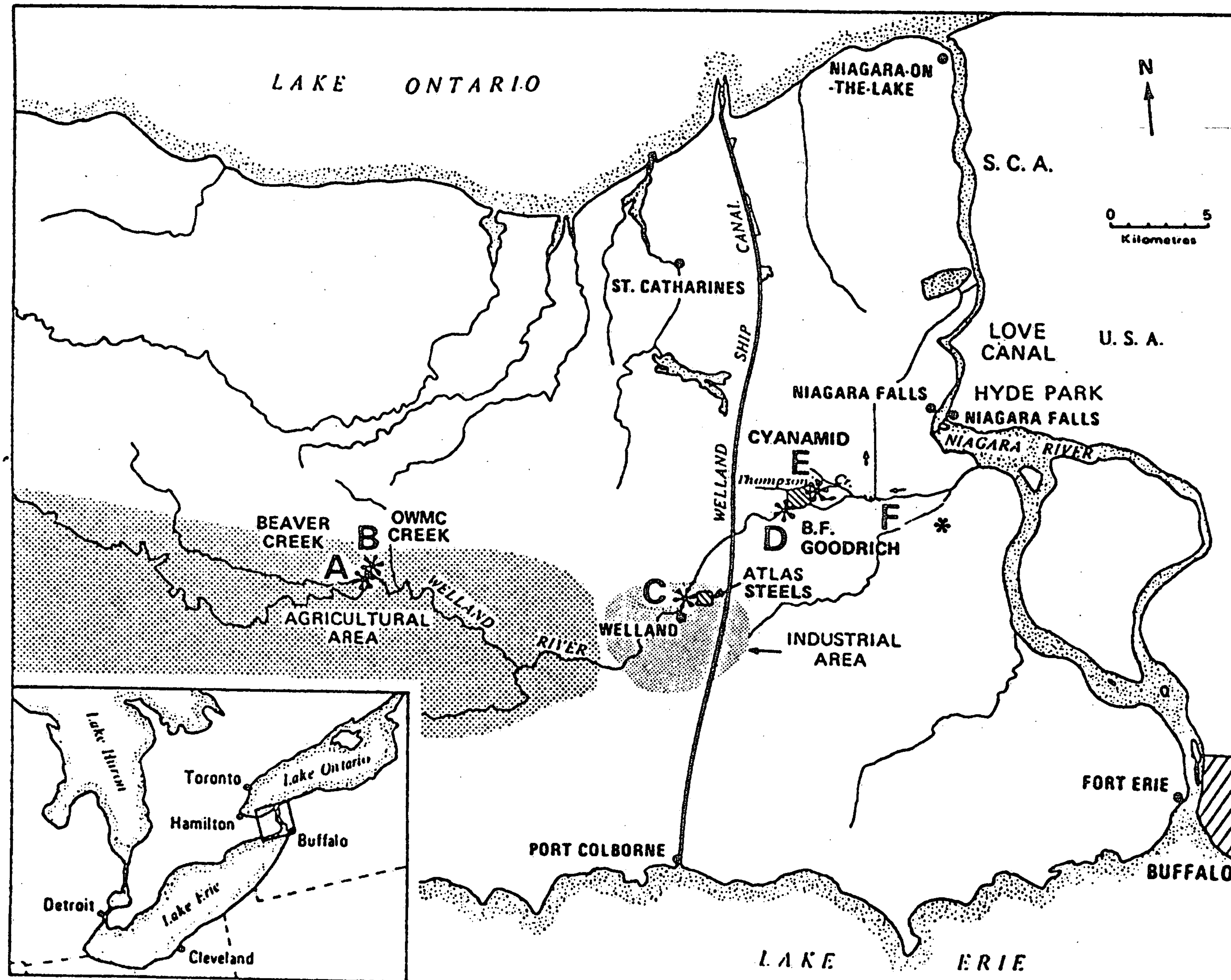
4 " - " not analyzed

5 not determined

Atlas Steels Data
Table 2

Sample No.	Cr	Pb	Fe	Ni	Zn	Cu
ATL 25S	260	160	9510	160	180	140
ATL 26N	1130	100	7900	90	130	70
ATL 28S	320	180	9900	220	200	140
ATL 31S	1150	230	15100	640	230	210
ATL 34S	1270	210	17500	860	190	250
ATL 37S	540	170	43100	1960	250	450
ATL 40S	780	760	35900	1300	1050	480
ATL 43S	530	470	25300	1610	820	470
ATL 46S	390	680	25600	1790	1030	610
ATL 49S	780	230	33200	1850	240	400
ATL 52S	1770	270	38200	2580	220	360
ATL 55S	1200	920	34600	2730	280	300
ATL 58S	2120	670	37600	3550	280	330
ATL 61S	2390	610	45000	2120	780	370
ATL 64S	4920	650	50500	4790	510	390
ATL 67S	5120	830	43000	4900	460	310
ATL 73S	2600	660	33000	2990	290	290
ATL 76S	1910	510	29300	2750	220	260

Figure 1



LAKE ONTARIO
NIAGARA-ON-THE-LAKE
N
S. C. A.
0 5
Kilometres
ST. CATHARINES
CANAL
SHIP
WELLAND
LOVE CANAL
U. S. A.
NIAGARA FALLS
HYDE PARK
NIAGARA FALLS
NIAGARA RIVER
CYANAMID
E
Thompson Cr.
BEAVER CREEK
B
OWMC CREEK
A
AGRICULTURAL AREA
WELLAND RIVER
F
D
B.F. GOODRICH
C
ATLAS STEELS
WELLAND
INDUSTRIAL AREA
FORT ERIE
PORT COLBORNE
BUFFALO
LAKE ERIE
Lake Huron
Toronto
Lake Ontario
Hamilton
Buffalo
Detroit
Lake Erie
Cleveland

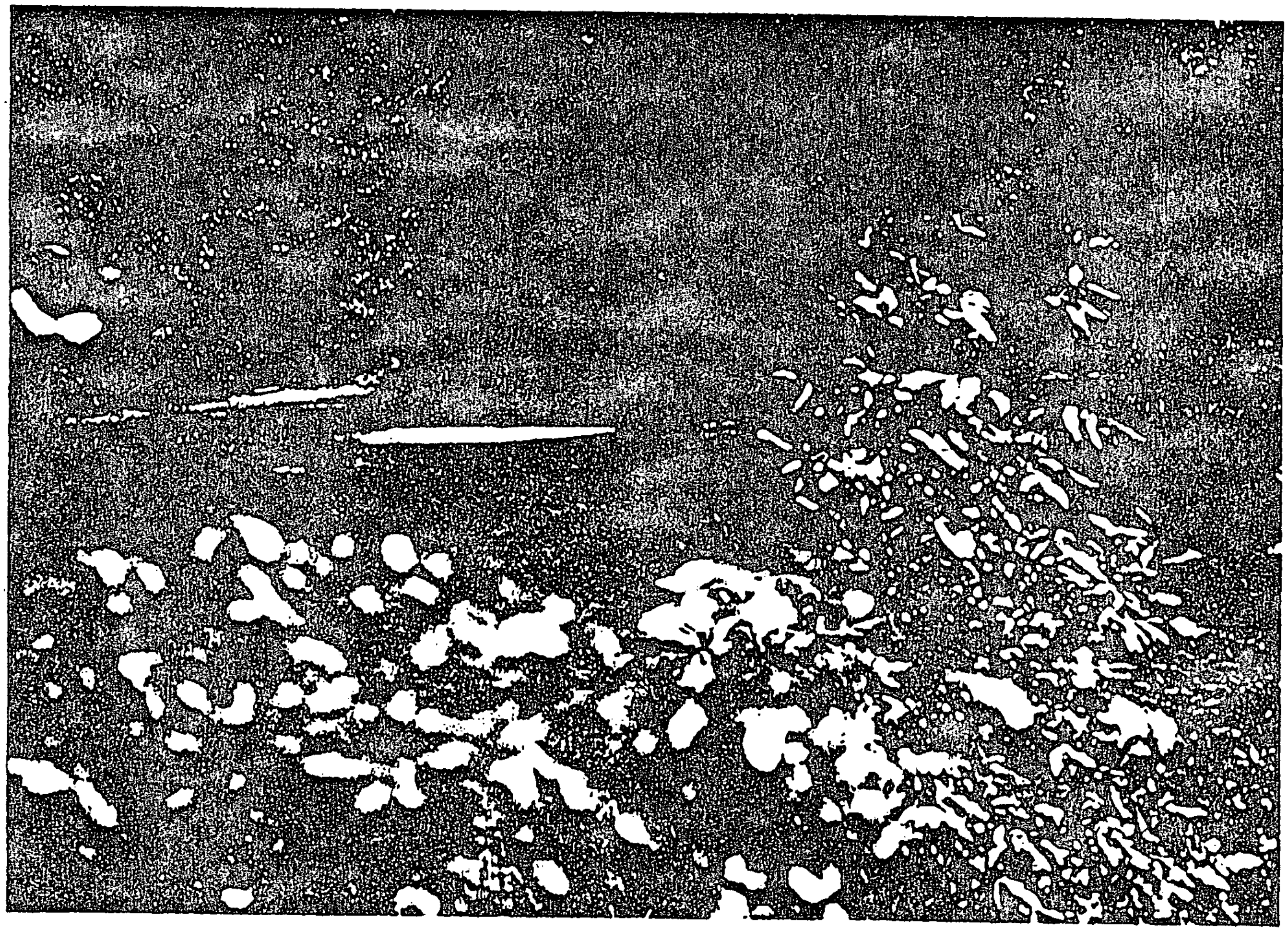


Figure 2

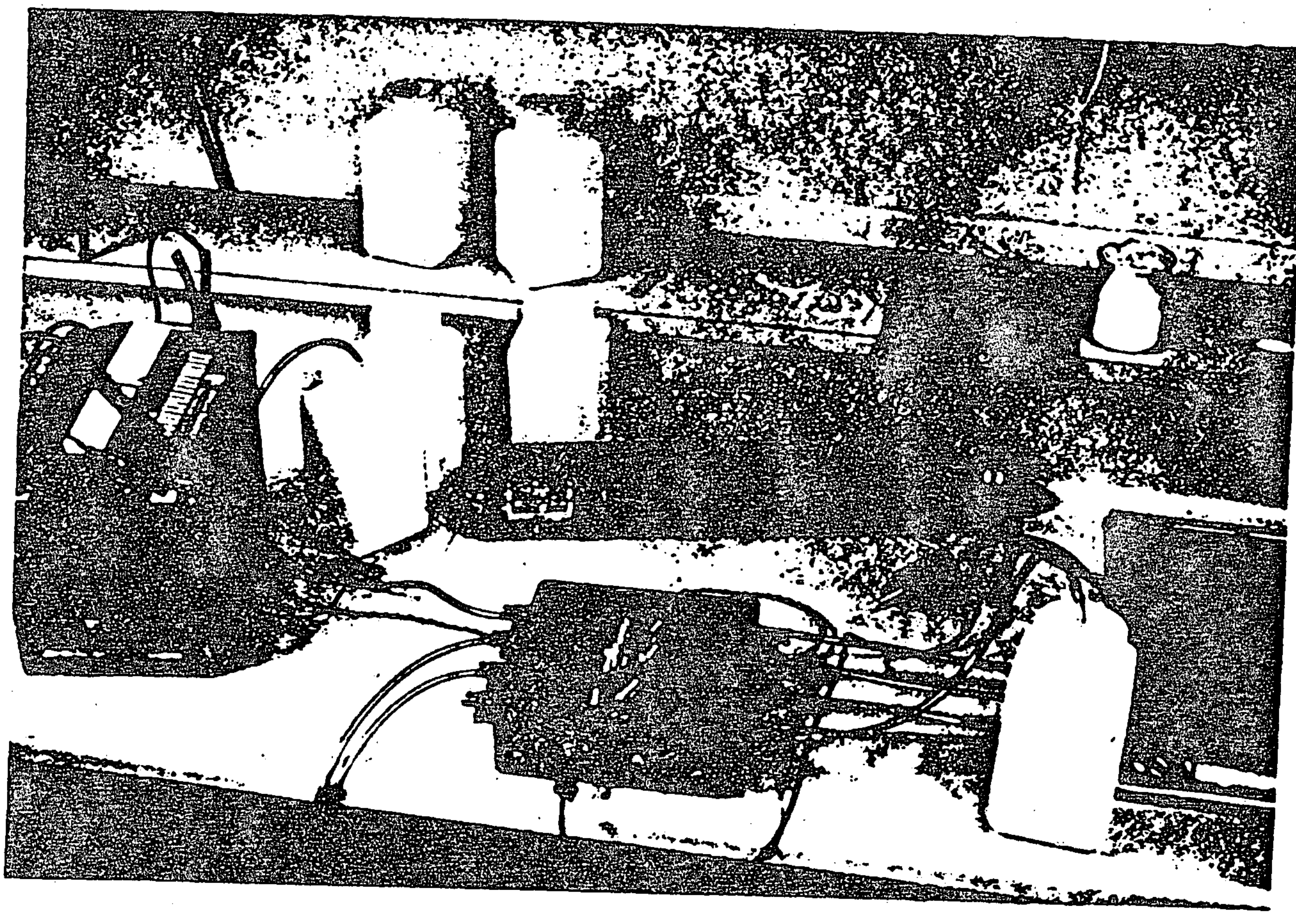
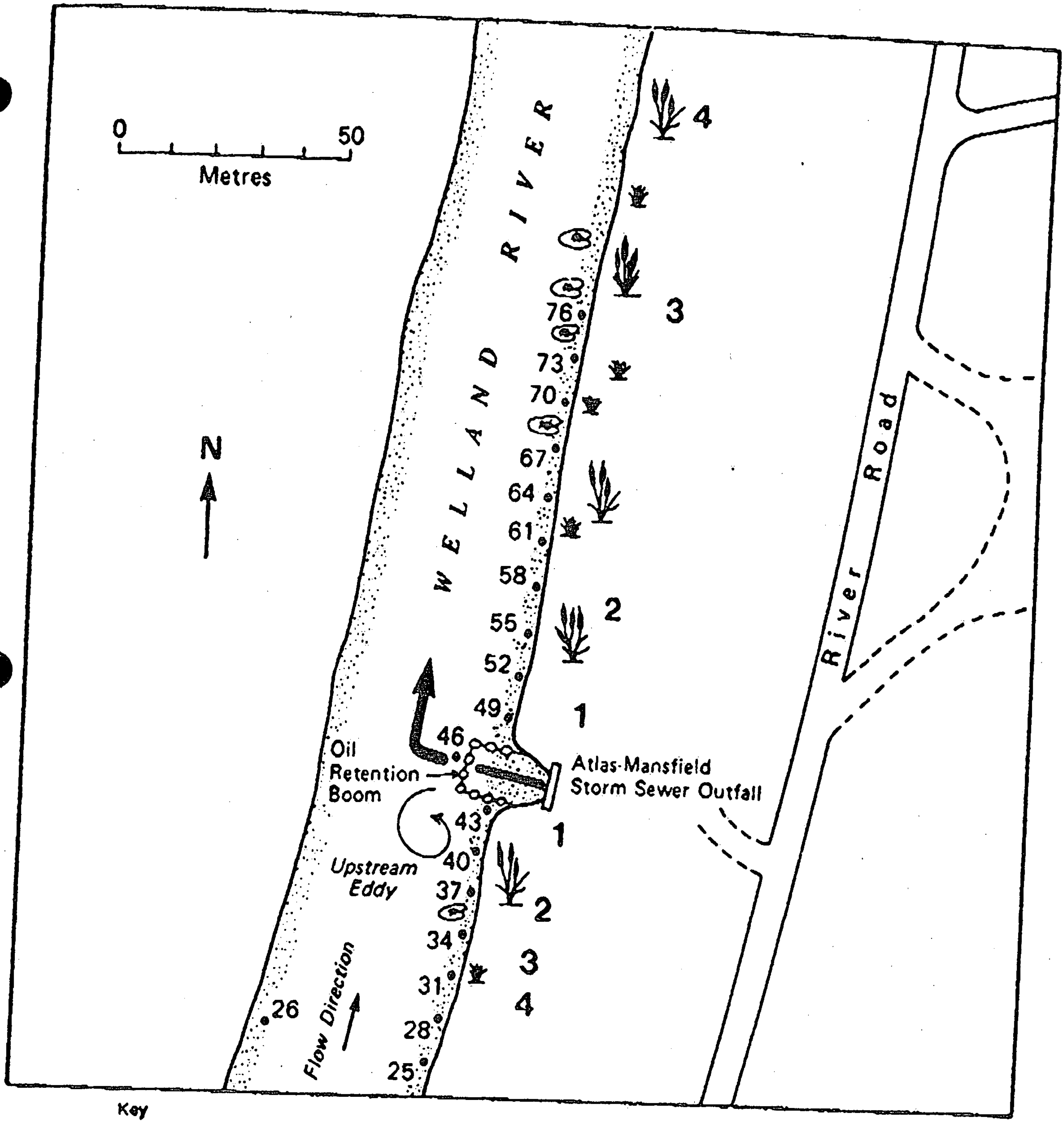


Figure 3



Key
1. Impact Zone (0 - 10m) no aquatic plants growing in water.
2. Primary Recovery Zone (10 - 15m). stunted Cattails and Sedges growing near waters edge.
3. Secondary Recovery Zone (15 - 85m). Cattails, Sedges, Arrowheads and Pondweeds
4. Tertiary Recovery Zone (85m -), same as above plus Cladophora and watermilfoil

...... Represents zone boundaries.

Legend

- Stunted Sedges
- Cattails
- Arrowheads
- Pondweeds
- Watermilfoil
- Cladophora

Numbers 25-76 refer to chemical analysis of sediments

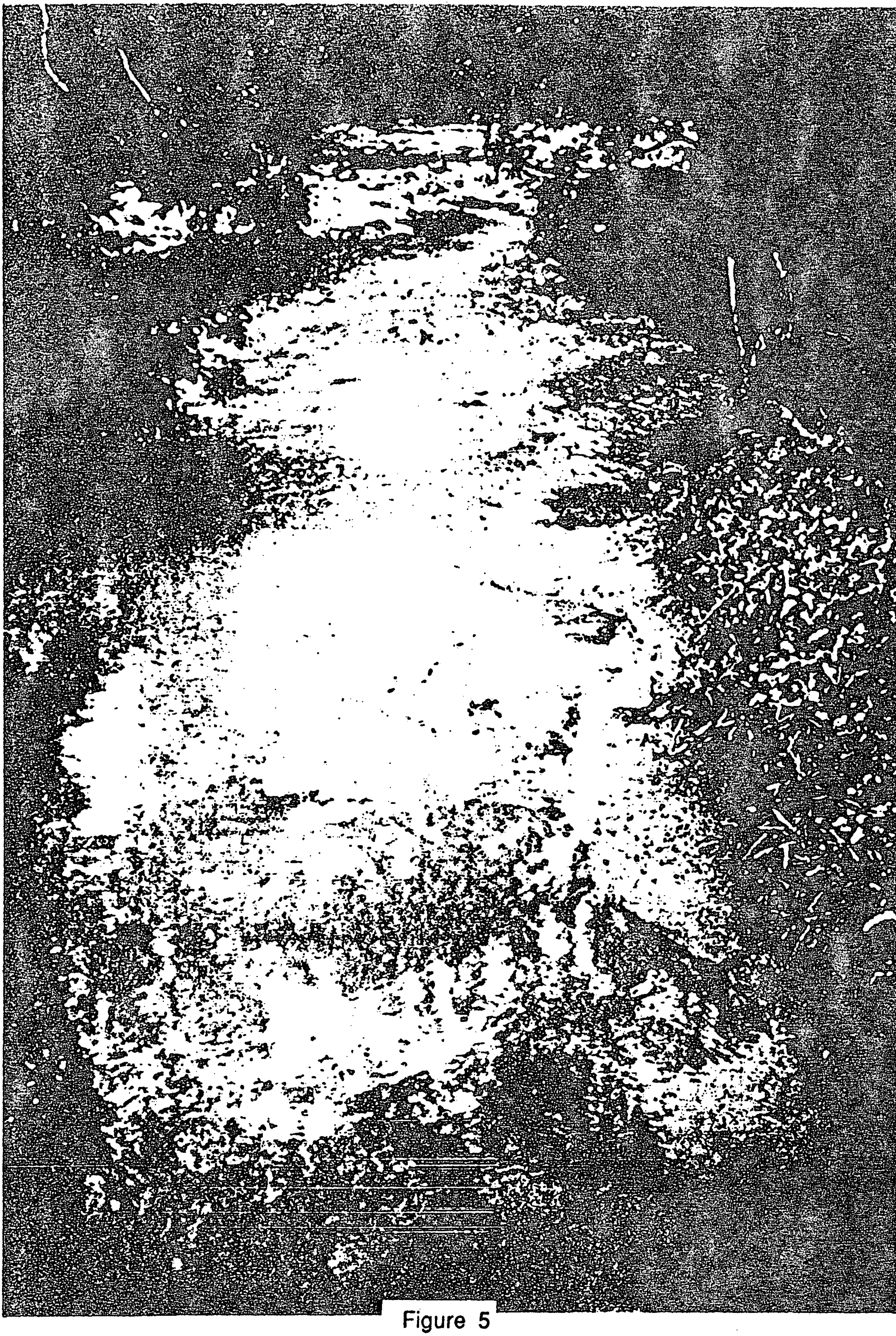


Figure 5

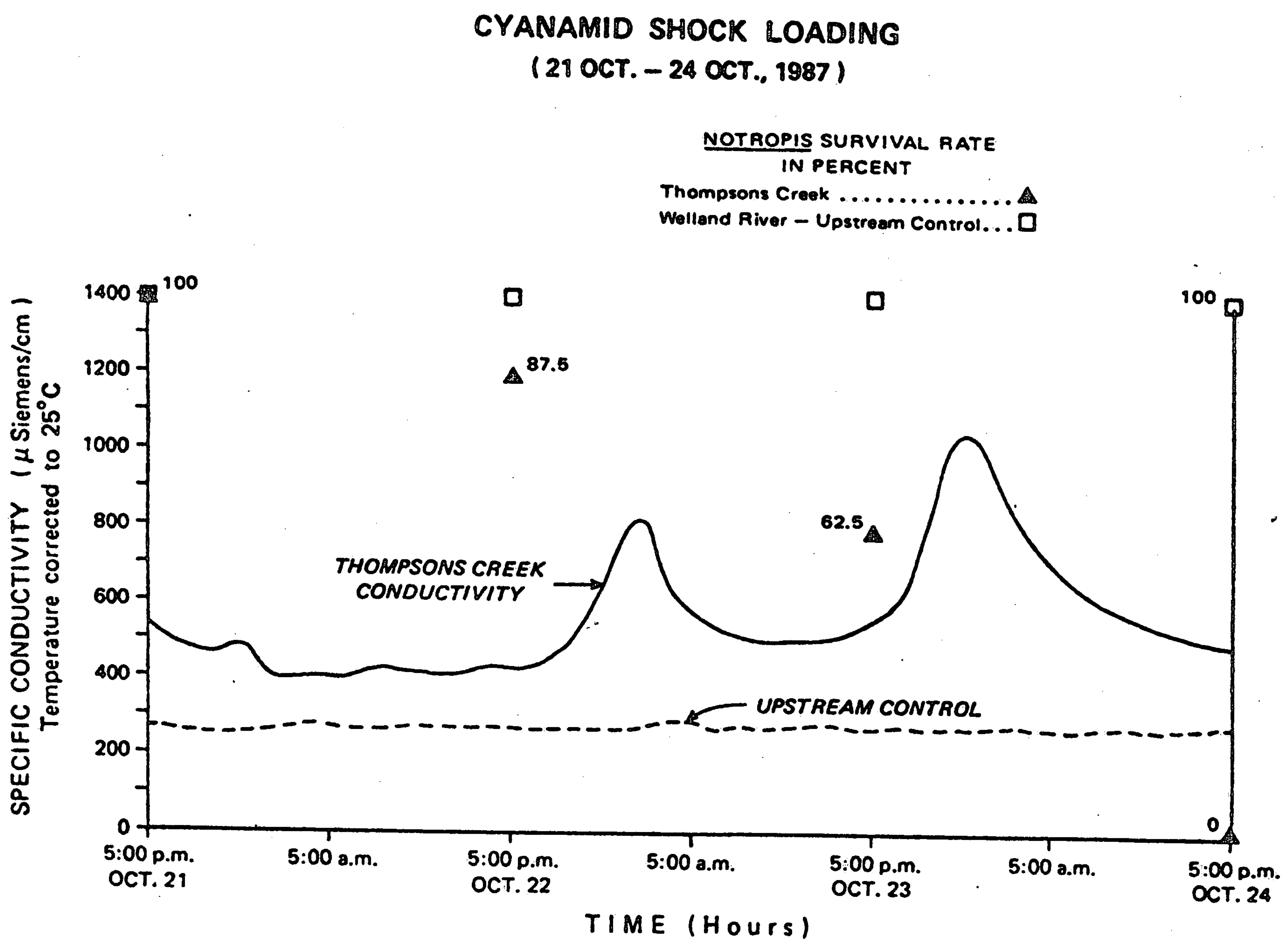

CYANAMID SHOCK LOADING
(21 OCT. – 24 OCT., 1987)
NOTROPIS SURVIVAL RATE
IN PERCENT
Thompsons Creek
Welland River – Upstream Control
100
87.5
62.5
100
0
THOMPSONS CREEK
CONDUCTIVITY
UPSTREAM CONTROL
SPECIFIC CONDUCTIVITY (μ Siemens/cm)
Temperature corrected to 25°C
1400
1200
1000
800
600
400
200
0
5:00 p.m.
OCT. 21
5:00 a.m.
5:00 p.m.
OCT. 22
5:00 a.m.
5:00 p.m.
OCT. 23
5:00 a.m.
5:00 p.m.
OCT. 24
TIME (Hours)

Figure 6

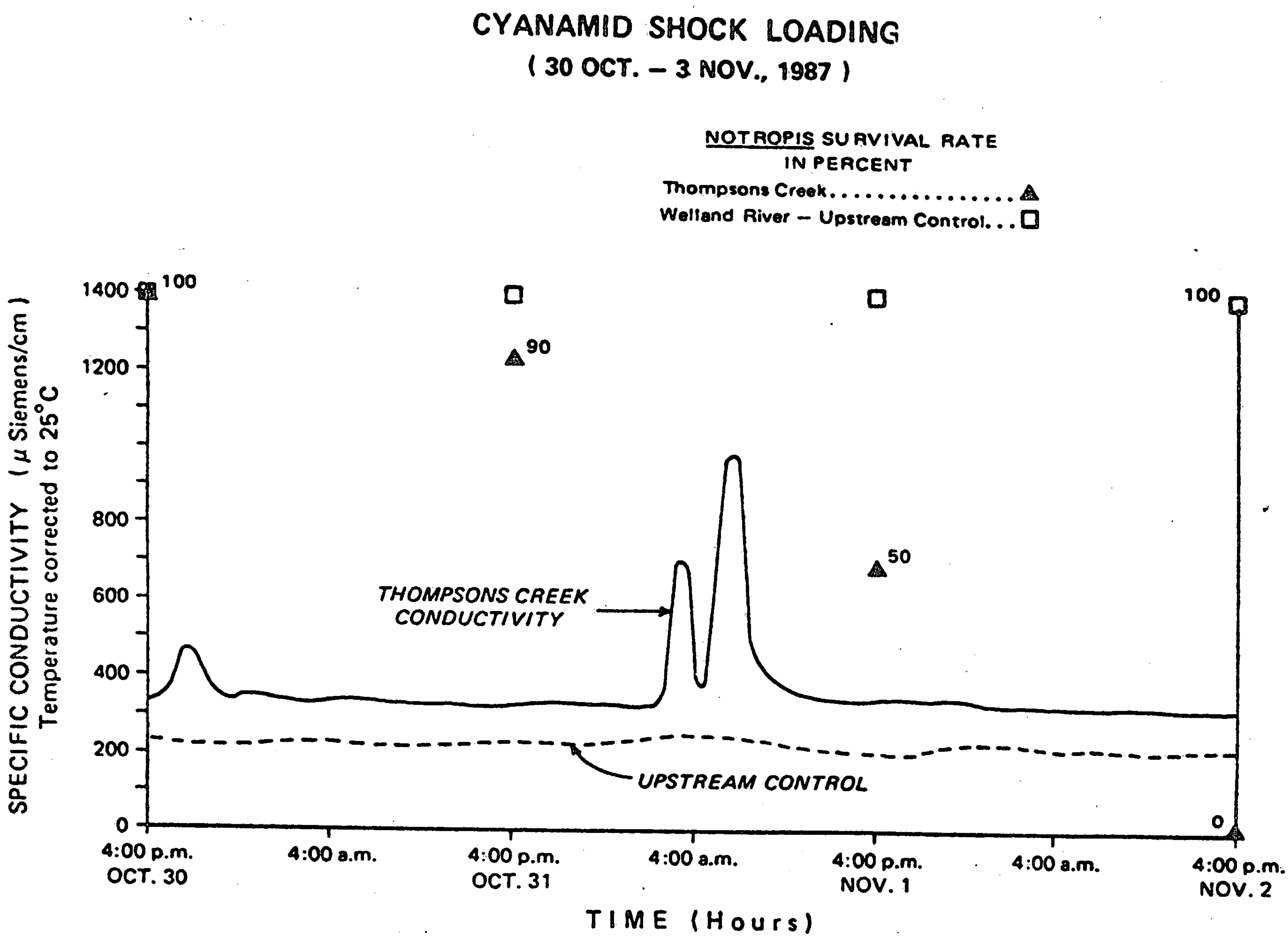

CYANAMID SHOCK LOADING
(30 OCT. – 3 NOV., 1987)
NOTROPIS SURVIVAL RATE IN PERCENT
Thompsons Creek
Welland River – Upstream Control
SPECIFIC CONDUCTIVITY (μ Siemens/cm)
Temperature corrected to 25°C
1400
1200
800
600
400
200
0
100
90
50
100
0
THOMPSONS CREEK CONDUCTIVITY
UPSTREAM CONTROL
4:00 p.m. OCT. 30
4:00 a.m.
4:00 p.m. OCT. 31
4:00 a.m.
4:00 p.m. NOV. 1
4:00 a.m.
4:00 p.m. NOV. 2
TIME (Hours)

Figure 7

ZONATION PATTERN OF HIGHER AQUATIC PLANTS AND EPIPELIC ALGAL SAMPLE SITES ON THE WELLAND RIVER

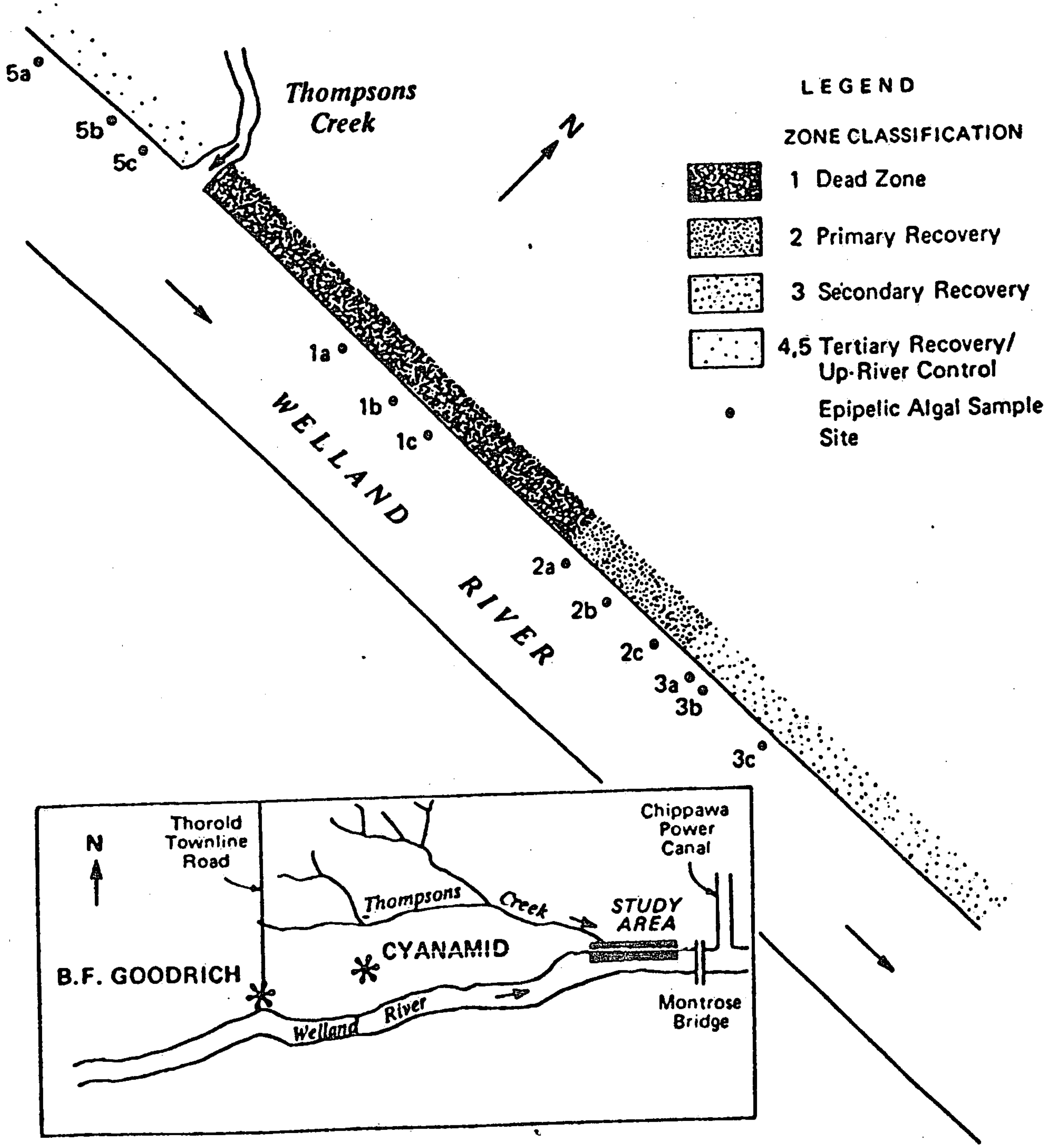


Figure 8

ATLAS STEELS SHOCK LOADING

(18 NOV. – 24 NOV., 1987)

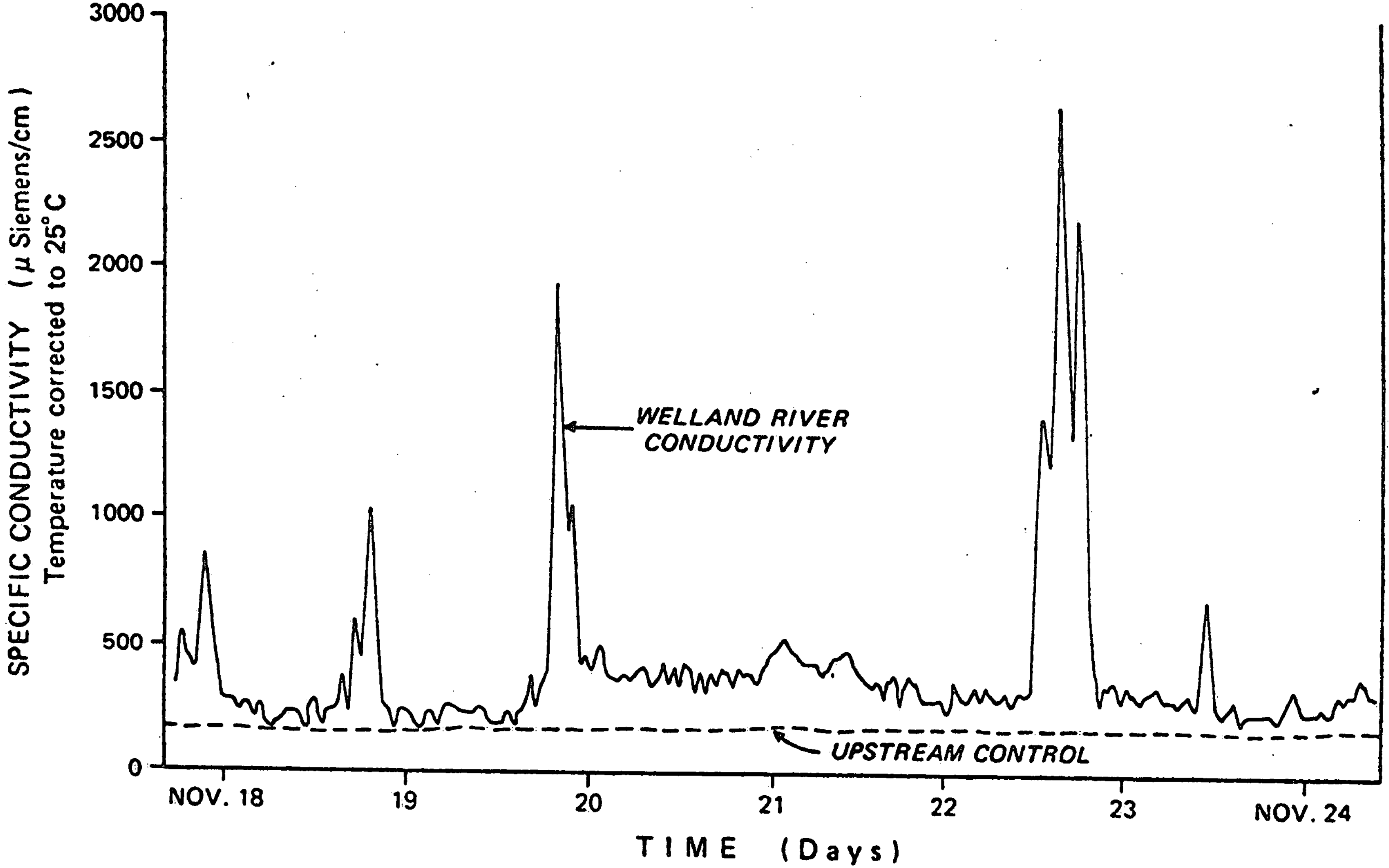


Figure 9