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Report to INTERNATIONAL JOINT COMMISSION United States and Canada

# GREAT LAKES WATER QUALITY Status of Pertinent EPA Research December 1974

National Environmental Research Center Corvallis, Oregon

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GREAT LAKES WATER QUALITY Status of Pertinent EPA Research December 1974



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This report was prepared under the auspices of the Great Lakes Research Advisory Board. The Board was created as a result of the United States/Canadian Great Lakes Water Quality Agreement of 1972. The agreement commits both countries to the improvement of the Great Lakes water quality and requires that pollution abatement measures be either completed or initiated by December 31, 1975. The eight-member board, principal scientific advisor to the International Joint Commission--United States and Canada and to the Great Lakes Water Quality Board, was organized to assure that research objectives of the Commission would be accomplished efficiently. Dr. A. F. Bartsch. Director of the U. S. Environmental Protection Agency's National Environmental Research Center at Corvallis, Oregon, serves as United States co-chairman of the Great Lakes Research Advisory Board.

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# INTRODUCTION

This report summarizes major segments of research activities the U.S. Environmental Protection Agency has completed or now has under way that relate to nitrilotriacetate (NTA), viruses, disinfection of municipal wastewater and the effects of polychlorinated biphenals (PCBs) on fish and fish products.

The summary is intended to highlight research areas which may have particular impact on objectives of the International Joint Commission as recommended in its 1973 annual report and should not be considered inclusive of all activities presently funded by EPA in the above subject areas.

During FY 1975, EPA plans to expend about \$2 million for continued research on:

- Nitrilotriacetate--\$300,000
- Viruses--\$600,000
- Disinfection of municipal wastewater--\$830,000
- Freshwater effects of PCBs on fish--\$300,000

# NITRILOTRIACETATE

#### Eutrophication

Research has been conducted at the Pacific Northwest Environmental Research Laboratory, Corvallis, Oregon, to determine the influences of NTA on eutrophication. Results indicate that in general NTA has no dramatic effects on algal growth rates. Any stimulatory or inhibitory effects appear to be related to the chelating properties of NTA and interaction with algal trace metal metabolism. There was no reduction in the NTA content of test medium when subjected to nitrogen-limited 21-day algal assays, indicating that NTA did not serve as a nitrogen source. Algal growth stimulation from phosphorus and secondary sewage effluents was much greater than any resulting from NTA.

Metals from river sediments near industrial and mining outfalls were solubilized by NTA more readily than those from lake sediments. Copper, iron, manganese, cadmium, and zinc were solubilized from sediments in the presence of NTA. However, copper from highly reduced lake sediments was not readily solubilized from Detroit River sediments.

In summary, NTA appeared to have no dramatic stimulatory or inhibitory effects on freshwater eutrophication processes (National Eutrophication Research Program, 1970). This is in contrast with the effects of NTA on marine estuarine systems where small amounts of NTA may produce a trace metals deficiency, thus limiting productivity (Erickson, Maloney, and Gentile, 1970). The long term effects of NTA in marine waters, however, might produce just the opposite impact. Since marine bacteria are capable of metabolizing NTA, it is possible that the end products of NTA degradation could serve as a nitrogen source, thus stimulating algal blooms in marine systems which are usually nitrogen limited.

Degradation Products and Energy Transfer Effects

Laboratory studies at the Robert S. Kerr Environmental Research Laboratory evaluated the probable impact of nitrilotriacetic acid on ground water. A report (Dunlap, Cosby, McNabb, Bledsoe, Scalf, 1973) indicated that the potential for pollution of ground water by NTA from detergents involved:

- possible introduction into ground water of undesirable organic degradation compounds of NTA, and
- possible transport of heavy metals into and through ground water by NTA in recharge water.

It was concluded that further clarification of these possibilities was necessary. Thus, studies of NTA degradation in anaerobic ground water environments were initiated in 1973.

Anaerobic ground water environment work is nearing completion. Results permit the following tentative conclusions:

> degradation of NTA in anaerobic subsurface environments is not likely to result in accumulation of significant quantities of undesirable organic degradation products in ground water, and

 the rate of NTA degradation in anaerobic ground waters will vary widely depending on microbial populations present and nutrient availability.

However, prediction of probable NTA degradation rates in specific anaerobic subsurface environments is not feasible at present since little information is available on these subsurface environments and their associated microbial communities.

Further work on NTA degradation by bacteria and yeasts in the marine environment is in progress at the Gulf Breeze Environmental Research Laboratory in Florida. Since this project is in its initial stage, considerable work remains to be done, but preliminary evidence indicates that there is some degradation of NTA in estuarine systems by the indigenous microbes. This has been evidenced through the evolution of <sup>14</sup>C labeled CO<sub>2</sub> from <sup>14</sup>C labeled NTA molecules.

Following the correction of minor problems with isotope analysis, a survey of the Pensacola Bay System will determine the differences in NTA degrading bacteria and yeast biomasses in polluted and non-polluted areas.

#### Toxicity

A grant awarded to the Academy of Natural Sciences of Philadelphia (Ruth Patrick, project officer) is designed to determine the effects of various concentrations of potential micronutrients, particularly NTA, on the efficiency of energy transfers and the structure of aquatic communities in artificial streams. Growth rates and biomass accumulations of various algal species are being studied and the efficiency of organics decomposition by bacteria and fungi in the presence of NTA is being determined. To date gas chromotographic procedures for NTA analysis have been refined to the point of detecting 0.02 mg/l, a level at the lower end of the range expected in natural habitats. NTA added to test streams at a maintained concentration of 0.2 mg/l induced no alteration of algal species composition or primary productivity over the control communities. The utilization of dissolved organic substances by heterotrophs in the system was not impaired.

The toxicity of NTA to various organisms in the aquatic food web has been tested at the National Water Quality Laboratory, Duluth, Minnesota. Experiments with <u>Daphnia magna</u> have shown that a strong negative correlation exists between water hardness and NTA toxicity (Biesinger, Andrew, and Arthur, 1974). That is, NTA was more toxic in soft water than in hard water.

Bioassay experiments of NTA, with copper and zinc added, confirmed earlier reports that chelates of copper and zinc with NTA are relatively nontoxic. This was also true for the amphipod <u>Gammarus pseudolimnaeus</u> and the fathead minnow <u>Pimephales promelas</u> (Arthur, Lemke, Mattson, and Halligan, 1974). The chronic no-effect level of NTA to the amphipods was 19 mg/1 and 54 mg/1 to the fathead minnows. This work has been completed and published.

Current year (FY-75) expenditures on NTA research amount to \$200,000. Projected expenditures for FY-76 total \$60,000.

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### VIRUSES

### Identification

EPA's National Environmental Research Center, Cincinnati, Ohio, is presently conducting research with waterborne viruses and their possible health hazards. During FY-75, work is proceeding in developing methods for concentration, recovery, and identification of viruses from water. Specifically, a grant has been let that will initiate development of an immunochemical method for identification and detection of waterborne viruses. Another project has been initiated to develop methods for identification and detection of viruses infecting blue-green algae.

The water supply program conducts health effects research concerned with the microbiological contaminants of water supplies. Work has been done to improve detection methods for viruses in raw and finished water. An integral part of this research is the design and implementation of epidemiological studies of contaminants that are suspected to be transmitted by drinking water. The water supply program is concerned with the improvement of virus detection methods and has determined that reliability in detecting enteric viruses appears to be greatly improved by concentrating the organisms from 400 or more liters of water. Emphasis is placed on three basic concentration methods that show promise:

- the flow-through gauze pad sampler technique,
- the membrane virus adsorption technique, and
- the insoluble polyelectrolyte (PE 60) method.

Tests are being conducted simultaneously under experimental conditions using poliovirus type 1 and concentration techniques with 400 liters or more of test water. A number of bench type experiments are planned to optimize and/or refine many of the procedural steps.

A study is under way to determine if viruses can be detected in finished drinking water and to evaluate and compare, under actual field conditions, the efficiency of the three virus concentration techniques. The study will relate the presence or absence of viruses in finished drinking water to treatment processes, water source and protection, total and fecal coliform densities, standard plate counts, and zoomicrobe populations.

### Epidemiology

An integral part of water supply research is the design and implementation of epidemiological studies of contaminants whose transmission by drinking water is suspected but not definitely proven. Two types of studies are under way:

- an intensive literature search relating to the minimal infective dose of enteroviruses and data collection on recovery of poliovirus from stools, sewage, streams, etc., and
- an objective determination of the age that children become infected with enteroviruses.

The water supply program maintains a tabulation on waterborne disease outbreaks. During 1971-72, 47 waterborne outbreaks resulting in 6,817 illnesses were reported in the United States. This is continuous research.

The air pollution health effects program at the National Environmental Research Center at Research Triangle Park, North Carolina, has in progress an epidemiological study to look at the effects of airborne biological contamination from sewage treatment plants. The study will focus on the relationship of airborne contaminants and the increased incidents of health problems in human populations living near municipal sewage treatment plants.

This is the second year of a three-year study. No results have been reported. If the findings indicate a correlation between health problems in areas surrounding treatment plants, additional work will be initiated to determine specific agents responsible for the health problems.

Prior to FY-74, \$703,000 was spent on this health effects research. In FY-74, \$300,000 was expended. For FY-75, \$600,000 is budgeted, with another \$600,000 planned for FY-76.

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# DISINFECTION OF WASTEWATER

Treatment Plant Effluent

The Advanced Waste Treatment Laboratory of the National Environmental Research Center in Cincinnati, Ohio, has completed and is currently involved in a number of projects relating to the disinfection of wastewater effluents. These studies can be classified into two major categories:

- effects of disinfection on aquatic organisms, and
- developments and demonstration of associated technology for effluent disinfection.

In-depth projects are scheduled to examine the state-of-the-art of these disinfectants:

- chlorine, hypochlorites, and chloramines, with dechlorination by sulfur dioxide, activated carbon, or bisulfite;
- bromine, bromamines, and bromine chloride;
- iodine;
- ozone;
- ultraviolet light; and
- chlorine dioxide.

Each disinfectant will be reviewed with regard to its chemistry in aqueous solutions. The bactericidal, virucidal, and cysticidal nature of each species will be compared, as well as its toxicity. Various external factors which impact the effectiveness of the disinfectant will be examined. Analytical methodology--such as principles of operation, chemistry, on-site monitoring of dosage and residual control--will be covered. Engineering and design aspects--including method of application, mixing chambers, contact chambers, safety measures and operation and maintenance--will be covered.

In the first phase of a demonstration project under way in Wyoming, Michigan, parallel disinfecting techniques for effluents from an activated sludge wastewater treatment plant are being evaluated for disinfection efficiency and residual toxicity. The processes under study include chlorination, chlorination with dechlorination, ozonation, and bromine chloride treatment.

An untreated fifth stream serves as a non-disinfected control. Results, which are preliminary and applicable to the waste discharged at this particular plant, indicate that the minimum bacteriological quality standard of 1,000 total coliforms and 200 fecal coliforms per 100 ml can be easily attained with bromine chloride and chlorine with and without dechlorination at residual disinfectant concentrations of less than 3.0 mg/l and a contact time of 30 minutes. At this particular plant, the ozone disinfection efficiency has not been this high.

The acute fish bioassay data indicate that chlorine is indeed toxic to various fish species, but that its toxicity is removed upon dechlorination with sulfur dioxide. Bromine chloride is also toxic, but to a lesser degree. The evaluation of ozone for possible toxicity is under way. Chronic fish bioassay determinations are in process to investigate the long-term effects of the disinfection processes on various fish species. This demonstration project represents the first time a comprehensive parallel comparision of various disinfectants and subsequent fish toxicity studies have been conducted under field conditions. The final results could have substantial impact on EPA policy regarding standards which will be published for wastewater effluent The second phase of this project, just getting under way, will follow the same format with effluent from a trickling filter plant. (Note: A workshop presenting research results from this project was held in October 1974, in Wyoming, Michigan.)

### Storm Water

A number of projects have been initiated to examine the various aspects of the disinfection of storm water. These studies have concentrated on techniques to obtain quick dosage of the wastewater through the use of various baffling and mixing techniques. Several combinations of disinfectants in conjunction with these physical techniques have been examined. As a result of these studies, rapid mixing and high turbulence have resulted in disinfection to the 1,000 total coliform per 100 ml level, with 1-minute contact time and 5 mg/1 chlorine dose.

In the near future, several other projects will demonstrate dechlorination procedures and flash mixing and contact systems. An evaluation of disinfection necessary for preparation of wastewater for ground water recharge is planned.

The total funding level for projects specifically related to disinfection prior to FY-75 amounted to \$2.1 million. Corresponding figures for FY-75 and FY-76 are \$630,000 and \$800,000. Many other projects examine various aspects of disinfection in a peripheral fashion.

#### Disinfectant Toxicity

Concurrently with the above demonstration program, additional effects studies are being conducted at the National Water Quality Laboratory to determine:

- safe concentrations of chloramines to Pacific salmon, trout, and crayfish;
- effects of chlorinated sewage on biota of Milwaukee Harbor and adjacent Lake Michigan;
- effects of chlorinated power plant condenser cooling water on rainbow trout and fathead minnows;
- toxicity of chlorinated municipal wastes to aquatic life;
- chlorination and ozonation products of municipal sewage;
- acute and chronic toxicity of chlorinated secondary sewage.

Results of the effects research have shown that chlorinated sanitary effluents are extremely toxic to confined aquatic organisms, especially fish. Most fish will avoid areas of higher concentrations when the discharge is continuous.

National Water Quality Laboratory criteria recommendations are:

- 0.002 mg/l total residual chlorine to protect salmonids and other more sensitive groups, and
- 0.01 mg/l total residual chlorine to protect warmwater fish and other less sensitive groups.

Through FY-74, EPA has expended \$886,000 for inhouse work relating to the disinfection of municipal sewage and its effect on aquatic organisms.

## FISH CONTAMINATION

EPA has completed a number of reports (National Water Quality Laboratory, 1973) that specify the effects of PCBs on freshwater organisms and aquatic ecosystems, including information on toxicity tissue residues and possible hazards to man. Data generated can be used to determine pollution standards for water, supplemental information for registration, and improving evaluation methods.

Continuous-flow and static bioassay tests have been conducted with several PCBs. Fish reproduction as a measure of relative toxicity has been determined for Arochlor 1221 (A1221), 1232, 1242, 1248, 1254, 1260, 1262, and 1268. Studies are continuing on the acute and chronic toxicity of various Aroclors to fish and invertebrates.

Two 9-month continuous-flow bioassays and several intermediate length continuous-flow tests were conducted to determine safe levels of Aroclor 1242, 1248, and 1254 for the fathead minnow Pimephales promelas and Aroclor 1248 for the flagfish Jordanella floridae. Calculated 96-hour LC50 values for newly-hatched fathead minnows were 7.7 µg/1 for Aroclor 1254 and 15  $\mu g/1$  for 1242. Three-month-old fatheads had a 96hour LC50 of 300 µg/1 for 1242. Reproduction occurred at and below 1.8  $\mu$ g/1 1254 and at and below 5.4  $\mu$ g/1 1242. Newly-hatched young were the most sensitive life stage. Growth of young fatheads was affected above 2.2 µg/1 1248. None survived above 5.1 µg/1 after 30 days. Young flagfish did not survive at 1248 concentrations above 5.1 µg/1 and did not grow well above 2.2 µg/1.

Fathead minnow fry less than 24-hours-old at the start of the test were exposed for 30 days to Aroclors 1248 and 1260. Median toxicity values of 4.35  $\mu$ g/l for 1248 and 2.5  $\mu$ g/l for 1260 were obtained. Total mortality was observed at 8.0  $\mu$ g/l and 7.0  $\mu$ g/l, respectively. Chronic tests have recently been completed with these Aroclors at concentrations of 3  $\mu$ g/l and below. While the data have not been analyzed statistically, there were no readily apparent effects on survival, growth, or reproduction.

The fathead minnows exposed to Aroclor 1248 and 1260 accumulated about 80 percent of the residue present after the 250-day exposure within the first 90 days. Aroclor 1248 was accumulated  $in_5$ lipids up to concentrations approximately 1.3 x 10 times that in water. Previous work at the National Water Quality Laboratory measured bioaccumulation factors for Aroclor 1242 and 1254. The data from these PCB studies indicate a consistent direct relationship betweeen the percentage of chlorine in the PCB and the bioaccumulation factor (inverse relationship with water solubility.)

Female fathead minnows in both exposures contained about twice as many PCBs on a wet weight basis as the males and showed a greater standard deviation. Males exposed to  $3.5 \ \mu g/l$  Aroclor 1248 accumulated 194 <u>+</u> 12  $\ \mu g/gm$  of the PCB on a wet weight basis. Since these variations can be accounted for largely by the greater percentage of lipids in the females, the data show that the residues cannot be adequately described throughout the bioassay unless the sex of the fish is included in the analysis.

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The results of this research indicate that Aroclors are very toxic. Chronically safe levels for fish and invertebrates are in the range of 1-5  $\mu$ g/1. Resultant residues are unacceptably high, and a much lower concentration near 1 mg/1 will be necessary to limit residue levels for the protection of the consumer--man or wildlife.

During the EPA Toxic Substances Hearings conducted in May 1974, the following items on the current use of PCBs were obtained during cross-examination of industry witnesses:

- admission that the production of Aroclor 1254 has not diminished since 1969--20,000 tons/year;
- typical industries using PCBs discharge 20 to 25 lbs/day into the environment; and
- retraction of industry contention that PCBs containing four or more chlorines are readily degraded in the environment.



### REFERENCES

Arthur, J. W., Lemke, A. E., Mattson, V. R., and Halligan, B. J. 1974. Toxicity of sodium nitrilotriacetate (NTA) to the fathead minnow and an amphipod in soft water. Water Res. 8:187-193.

Biesinger, K. E., Andrew, R. W., and Arthur, J. W. 1974. Chronic toxicity to NTA (nitrilotriacetate) and metal-NTA complexes to <u>Daphnia</u> <u>magna</u>. Jour. Fish. Res. Bd. Can. 31:486-490.

Dunlap, W. J., Cosby, R. L., McNabb, J. F., Bledsoe, B. E., and Scalf, M. R. 1971. Investigations Concerning Probable Impact of Nitrilotriacetic Acid on Ground Waters. EPA Water Poll. Cont. Research Series 16060 GHR 11/71.

Erickson, S. J., Maloney, T. E., and Gentile, J. H. 1970. Effects of nitrilotriacetic acid on the growth and metabolism of estuarine phytoplankton. Jour. Water Poll. Cont. Fed. 42(8):R329-335.

National Eutrophication Research Program. 1970. Field and laboratory investigation to evaluate the influence of nitrilotriacetate (NTA) on eutrophication. Report to the Commissioner of Federal Water Quality Administration. Unpub. rpt.

National Water Quality Laboratory. 1973. Summary of Research Findings for Fiscal Year 1973. U.S. Env.

