Research and Development

EPA-600/S3-84-064 June 1984

# ♣EPA Project Summary

# Chemical and Biological Studies Related to the Water Quality of St. Louis Bay of Lake Superior

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This study was a cooperative effort among the University of Wisconsin-Superior, University of Minnesota-Duluth, and U.S. EPA Environmental Research Laboratory-Duluth to develop and evaluate effluent toxicity screening methods and test methods and protocols for deriving site-specific water quality criteria. The principal components of the study were to include: (1) a chemical characterization of the main discharges to the St. Louis River and Harbor, (2) persistence of toxic pollutants in the St. Louis River and Harbor, (3) a description of the exposure times for various components of the ecosystem, (4) bioassays with St. Louis River water ad resident species. (5) an assessment as to the degradation of the biologic community of St. Louis Harbor, and (6) a modeling framework to address items 1 through 5.

Because persistent toxic pollutant concentrations were not found in the Western Lake Superior Sanitary District (WLSSD) effluent and no persistent open water pollutant problems were apparent, this study was ended. Following are a series of reports on work completed.

This Project Summary was developed by EPA's Environmental Research Laboratory, Duluth, MN, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

#### Introduction

St. Louis Bay of Lake Superior provides a unique opportunity to study a natural

ecosystem and related observed response to pollutants to laboratory testing effect endpoints and observations. To understand a pollutant's cause and effect relationship in such a system, it must be studied in sufficient depth to understand the controlling factors. To this end, several on site (field) and laboratory studies were undertaken to quantify possible pollutant impacts and resulting biotic responses of the bay ecosystem.

Such research is needed to provide a basis for the U.S Environmental Protection Agency's (EPA) Office of Water to provide guidance to the states on the modification of national water quality criteria to site-specific situations, and the control of complex effluents through the National Pollution Discharge System. The EPA Great Lakes National Program Office also needs information on the causes of pollution of St. Louis Bay and the impact of the bay on western Lake Superior

The primary objectives of this research project were: (1) field test the EPA guidelines for deriving site-specific water quality criteria, (2) obtain data on the relationship between toxicity testing of a complex effluent and receiving water biotic response, and (3) evaluate the usefulness of water quality criteria to protect a Great Lakes ecosystem.

To meet the above objectives, three conditions must have existed. The first is that a point source discharge to the bay had to be at least chronically toxic, the toxic components of the effluent had to be identified, and the bay biota had to be impacted by the effluent. Because the Western Lake Superior Sanitary District (WLSSD) discharge, containing both

treated domestic and industrial wastes. appeared to meet the above conditions, it was selected for initial study. It is the largest single point discharger to the bay, its final effluents had exhibited toxicity in the past and some fish kills had occurred in the embayment near its discharge pipe During 1982 studies to chemically characterize the WLSSD effluent, determine its toxicity and trace its movement in and out of the bay were initiated Other studies were initiated to provide a water chemistry and biological baseline for the bay from which present and future pollutant impacts on the bay, and the bay's impact on Lake Superior, could be determined A literature search of all studies relevant to St. Louis Bay was also begun. Information gained from these first-year efforts were necessary to determine if the primary objectives of this research project were achievable and, if achievable, to plan subsequent studies.

This project was undertaken as a cooperative effort of the U.S. EPA Environmental Research Laboratory-Duluth, University of Minnesota-Duluth, and University of Wisconsin-Superior. Following are reports on individual research tasks undertaken in 1982.

### Results and Conclusions--St. Louis Bay

#### Water Chemistry Surveys

At the six sites, in the small embayment near the WLSSD wastewater treatment plant, ammonia, alkalinity, total phosphorus, and chloride were higher than in the control embayments.

The fraction of WLSSD effluent, estimated from chloride concentration was 0.20-0.25 in the three sites closest to the discharge pipe and 0.05-0 10 in the three sites farthest from the discharge pipe. Ammonia and total phosphorus appear to have a substantial sediment source in the small embayment near WLSSD.

Nutrient input budgets for St. Louis Bay revealed that 90% of the alkalinity, ammonia and total phosphorus loadings were derived from the St. Louis River with the remainder originating from WLSSD. However, high chloride concentrations in the WLSSD effluent contribute 43% of the Cl<sup>-</sup> loading to St. Louis Bay, compared to 57% from the St. Louis River.

Comparison of the total phosphorus input budget for 1982 with a similar budget for 1972 revealed that the WLSSD sewage treatment plant released one-fifth the total phosphorus that was

released by the nine sewage treatment plants operating in 1972

Phenol concentrations decreased from 8 to 9  $\mu$ g L<sup>-1</sup> in the mid-1970s to 3  $\mu$ g L<sup>-1</sup> in 1982.

The mean total phosphorus at site L (downstream from the present WLSSD plant) decreased from 110  $\mu$ g L<sup>-1</sup> between 1972 to 1979 to 75  $\mu$ g L<sup>-1</sup> for 1979 to 1982.

The mean ammonia concentration at site L decreased from 0.259 mg L<sup>-1</sup> (pre-1979) to 0.116 mg L<sup>-1</sup> after 1979.

### Benthic Invertebrate Surveys

The benthic invertebrate surveys demonstrated noticeable differences between the WLSSD discharge bay and two bays (controls) upstream. The discharge bay contained fewer types of organisms and these are considered more tolerant of domestic effluents. The differences between the bays were less noticeable in October than in June or August.

## Phytoplankton and Zooplankton Surveys

The Duluth-Superior Harbor is a complex system for pelagic sampling. Not only is the bathymetry complex, with the extensive shallows plus the deep dredged ship channels, but the interactive flows of the St. Louis River and seiche currents from Lake Superior make point samples a function of many variables. In the shallows, particularly, the range of seasonal change can be extreme Within this context, examination of the plankton data from Summer 1982 shows no adverse influence of the effluent from the WLSSD plant.

### WLSSD Effluent Toxicity and Characterization Effluent Toxicity

The effluent was intermittently acutely toxic to aquatic organisms (fish and invertebrates) in toxicity tests. Behavioral monitoring of fish continuously exposed to the plant effluent was used to identify periods of effluent toxicity.

Increases in fish locomotor and respiratory activity correlate with fish mortality in bioassays of grab samples. Some possible causes of observed toxicity were thought to be related to elevated total residual chlorine or carbon dioxide concentrations resulting from changes in wastewater treatment in response to changes in influent conditions.

It is recommended that any future bioassays of WLSSD effluent, or the

effluent from other treatment plants, be complemented with chemical analyses of total chlorine, pH (immediate and after extended aeration), carbon dioxide, alkalinity, and hardness. If possible, these tests should be coupled with sensitive aquatic organism behavioral monitoring to identify episodic periods of toxicity.

### Effluent Characterization

A comparative qualitative analysis was made of the WLSSD effluent and influent. and a similar analysis was made of the effluent from the largest single contributor of industrial type organics (a pulp and paper industry) to the WLSSD influent The isolation and concentrations in composite samples were done in threes to reflect the acidic, neutral, and basic functionalities in the components analyzed using mass spectroscopy. The mass of data is presently being incorporated into a three x three matrix (3 analyses and 3 sample sites) based on functionality. When completed, an interpretation of the meaning and significance of the data will be made.

Because chlorophenols originating from WLSSD had been previously traced within the bay and into Lake Superior, a gas chromatography with electror capture detection procedure aimed a sensitivity and a second procedure with liquid chromatography with a variable wavelength that would aid the identification of chlorophenols in complex mixtures were developed.

A detailed report containing the methods used in effluent characterization and raw data, and chlorophenol analysis procedures are available on request.

#### **Conclusions**

- The water quality of the St. Louis Harbor has improved. Much of the improvement can be attributed to the onset of the operation of the present WLSSD wastewater treatment plant.
- There was only a slight impact or the benthic invertebrate community from the WLSSD outfall.
- Survey data indicate that phytoplankton and zooplankton were not demonstrably impacted by the WLSSD effluent.

- 4. The WLSSD plant is currently treating its waste to a higher degree than the 1 mg/L phosphorus limit. The concentration in the main channel opposite the plant has decreased by a factor of three since 1973.
- 5. The WLSSD discharge was occasionally acutely toxic. It appears that some toxic discharges are related to changes in treatment processes and plant operations in response to special waste treatment needs resulting in high residual chlorine or carbon dioxide concentrations in the effluent. Data indicate that at times the mixtures of the WLSSD plant effluent and bay would be acutely toxic in the immediate vicinity of the discharge pipe but not impact the rest of the bay because of a high dilution ratio.
- 6. The primary objectives of this research project were not attainable at this site because persistent toxic pollutants were not found in the WLSSD effluent and no persistent open water pollutant problems were apparent.

### **Bibliography**

Devore, P. 1983. An Annotated Bibliography of Environmental Research Conducted Within the St Louis River Estuary 1903-1982. [Order No NTIS PB83-261-693] (EPA-600/S3-83-092). This report is intended as a tool for people to locate specific types of studies conducted within St. Louis Bay and was an attempt to compile and review all the physical, biological, and chemical studies related to the bay.

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The complete report, entitled "Chemical and Biological Studies Related to the Water Quality of St. Louis Bay of Lake Superior," (Order No. PB 84-195 379; Cost: \$14.50, subject to change) will be available only from:

National Technical Information Service 5285 Port Royal Road Springfield, VA 22161 Telephone: 703-487-4650 The EPA Project Officer can be contacted at: Environmental Research Laboratory

U.S. Environmental Protection Agency 6201 Congdon Blvd. Duluth, MN 55804

☆ U.S. GOVERNMENT PRINTING OFFICE, 1984 — 759-015/7734

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United States Environmental Protection Agency Center for Environmental Research Information Cincinnati OH 45268

Official Business Penalty for Private Use \$300

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