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Project Summary

Toxicity Reduction Evaluation at the Patapsco Wastewater Treatment Plant

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A water quality-based toxics control process in wastewater treatment is being established by the U.S. EPA to support the development of discharge permits, including effluent toxicity measurements. Upon confirmation of a toxics water quality problem, a toxics management program, referred to as a Toxicity Reduction Evaluation (TRE), can be implemented to identify and control the sources of the effluent toxicity. The goal of a TRE is to determine the steps that are required to reduce effluent toxicity to acceptable levels.

A municipal TRE research study was recently completed at the Patapsco Wastewater Treatment Plant in Baltimore, MD. The purpose of the study was to develop and evaluate procedures to assess toxicity problems at a municipal treatment plant receiving wastewater from a wide range of industrial sources and to develop practical approaches to control the toxicity. The Patapsco study revealed high levels of toxicity entering the plant as measured by *Ceriodaphnia dubia* (acute and chronic), *Mysidopsis bahia* (acute), and Microtox™* (acute) tests. The *C. dubia* test was the most sensitive indicator of influent and effluent wastewater toxicity. While the Patapsco Plant met its permit requirements for conventional pollutants and achieved major reductions in wastewater toxicity, substantial acute and chronic toxicity as measured by *C. dubia* and *M. bahia*, was continuously present in the unchlorinated secondary effluent. Substantial Microtox™ toxicity also was intermittently present in the unchlorinated secondary effluent.

Characterization of the influent and effluent toxicity revealed that most of the toxicity was associated with nonpolar organic compounds that adsorbed strongly to the solids in the wastewater. Intermittent and modest amounts of toxicity were also associated with volatile organics, ammonia, and polar organic compounds. Identification of the specific organic compounds causing the toxicity was not achieved using standard gas chromatography/mass spectroscopy (GC/MS).

Batch treatability tests on selected industrial discharges using acute toxicity assays as performance indicators provided a method for identifying and ranking the industrial discharges as potential contributors to the Patapsco plant's wastewater toxicity. Efficient solids separation treatment of the batch test effluent removed most of the acute toxicity.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, 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

The Patapsco Wastewater Treatment Plant in Baltimore, MD, is a municipal oxygen activated sludge plant treating both domestic-commercial wastewaters and discharges from approximately 100 industries. The plant is well-operated and meets its permit requirements for conventional pollutants. Long-term historical data

*Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

from Microtox™ tests and limited data from *C. dubia* bioassays, however, revealed high levels of toxicity in the wastewaters entering the plant and substantial toxicity pass-through in the plant's effluent. Thus, in January 1986, the U.S. EPA and the City of Baltimore entered into a cooperative agreement to perform a research TRE study at the Patapsco Plant. The TRE was initiated in April 1986, and completed in September 1987, and represents one of the first case histories of a toxicity management program at a municipal wastewater treatment plant. During the study, the plant, which is designed for 70 mgd, was operated at approximately 45 mgd with its oxygen bioreactors employing an average 14-day mean cell residence time in the warm water season and approximately a 17-day mean cell residence time in the cool water season

Research Objectives

The objectives of this TRE were:

- to evaluate the fate and impact of acute and chronic toxicity during treatment and the pass-through of toxicity in the plant effluent;
- to characterize the toxicity as to broad classes or types of toxics and, if possible, to identify the specific compounds causing the toxicity; and
- to develop procedures to trace the toxicity to its sources and evaluate its treatability both at the central treatment plant and through pre-treatment.

Research Approach

The first element of the TRE involved the characterization of plant operations and performance using conventional pollutant monitoring, monitoring for specific priority (toxic) pollutants, and evaluation of acute and chronic influent and effluent wastewater toxicity. The collection of the composite wastewater samples used in monitoring were scheduled to account for the average process hydraulic detention time of the plant (i.e., secondary effluent composites were collected 8 hr after primary effluent composites). The toxicity assays were *C. dubia* (acute and chronic), *M. bahia* (acute), and Microtox™ (acute) tests. The toxicity testing end points used in the study included the LC_{50} defined as the wastewater effluent concentration in percent effluent in the test causing lethality to 50% of the test population in the established test time, the EC_{50} defined as the effluent concentration in percent effluent in the test causing a 50% reduction in the observed test effect (light phosphorescence) in the established test time, and the chronic value (ChV) expressed as percent effluent and defined as the geometric mean between the no observable effects (NOEC) and the lowest observable effects concentration (LOEC) in the life cycle test.

The characterization of plant operations included biomass oxygen and substrate (COD) uptake rates and adenosine triphosphate (ATP) measurements in laboratory studies to indicate potential inhibition impacts on the plant's biomass. Because the domestic-commercial and industrial wastewater sources are largely separated between two sewers, the characterization study was able to evaluate the relative importance of the two wastewater sources to the wastewater toxicity in the treatment plant. Using the toxicity data for the influent and effluent wastewaters, possible relationships (Pearson's Product-Moment Correlation) among the three toxicity bioassays and relationships between the Microtox™ toxicity and other conventional performance indicators were also evaluated. The objective was to evaluate less expensive monitoring alternatives (Microtox™ and conventional performance indicators such as oxygen and COD uptake rates) as possible surrogates for the classical bioassays in the prediction of toxic events.

A second element of the TRE approach involved characterization of the toxicity in the Patapsco influent and effluent wastewaters. Wastewater fractionation/identification procedures were used to indicate the general classes of toxics causing the toxicity and to attempt to identify by standard analytical techniques the specific toxics causing the toxicity. The fractionation procedures evaluated the amounts of toxicity removed by aeration, filtration, ammonia stripping, C_{18} solid phase extraction with methanol elution of non-polar organics, and ion exchange separation for cations and anions. The toxicity of the residual compounds (i.e., polar organic compounds not removed by C_{18} fractionation) was also estimated. Because the fractionation procedure is conducted as a series of bench-scale treatment tests, the results of the procedure provided insight into the treatability of the toxicity.

The third element of the TRE approach involved an evaluation of industrial wastewater sources to determine their relative contribution to the toxicity in the plant effluent and the treatability of the industrial wastewater toxicity by the plant's biomass. A toxicity treatability screening procedure, developed during the TRE, was applied to five of the largest industrial dischargers to the Patapsco Plant. The tc icity treatability screening procedure us batch treatability tests that simulated t operation of the central treatment pla The tests evaluated the contributions of t industrial wastewaters with respect to hibition of the plant's biological process and to toxicity pass-through in the plan effluent. The individual industrial was waters were mixed in 2-L batch reactc with central plant biomass and eith primary effluent or nontoxic synthe wastewater and then biologically treated a batch test food-to-mass ratio equivale to the nominal operating food-to-mass ra in the Patapsco plant. After aeration, t batch test mixed liquor was filtered throu a coarse filter to simulate seconda sedimentation.

Parameters used to evaluate t treatability of the industrial wastewaters cluded biomass activity as measured changes in oxygen uptake and solut COD substrate uptake rates and efflue toxicity as measured by Microtox™ and *dubia*. Because the plant sludges were cinerated, toxicity assays and speci chemical analyses were not applied to t batch test sludges. The wastewater fra tionation/identification procedures we also used to characterize the toxicity of t batch test effluents.

Results

Plant Performance

A review of the operation and perf mance data revealed that the Pataps Plant performed well in terms of conve tional pollutant treatment during the TI period of May 1986 to January 1987. T effluent suspended solids typically vari from 20 to 27 mg/L, while the BOD_5 in t effluent averaged 9 and 16 mg/L for t warm and cool water seasons, respecti ly. The plant's effluent quality met t plant's existing permit requirements a the pass-through of toxicity was not cat ed by plant operation or performan deficiencies.

The influent to the Patapsco plant hibited high levels of acute and chronic t icity as measured by the 7-day static *dubia* (acute-chronic), 96-hr static *M. bal* (acute), and Microtox™ (acute) tes Primary sedimentation did not redu wastewater toxicity. Major reductions in t icity (Table 1) were achieved by the tivated sludge process; however, substa tial acute and chronic toxicity as measur by the *C. dubia, M. bahia,* and Microto tests passed through in the Patapsco fluent. The *C. dubia* test was the most se

Table 1. *Toxicity Reduction at the Patapsco WWTP*

	Microtox™	M. bahia	C. dubia	
Expressed as	*5-min EC_{50}*	*96-hr LC_{50}*	*48-hr CL_{50}*	*Chronic 7-day ChV*
Effluent Toxicity (as % effluent)				
Mean ∓ SD, %*	*79.3 ∓ 23.4*	*47.6 ∓ 23.1*	*6.3 ∓ 4.6*	*2.5 ∓ 2.1*
N Samples	*40*	*44*	*45*	*45*
% Toxicity Reduction†				
Mean ∓ SD	*87.7 ∓ 12.2*	*55.5 ∓ 16.8*	*60.7 ∓ 30.4*	*62.5 ∓ 31.1*
N Samples‡	*37*	*12*	*13*	*12*

**SD is the standard deviation.*
† % Toxicity Reduction (TR) =

$$\frac{\text{TU Primary Effluent - TU Secondary Effluent}}{\text{TU Primary Effluent}} \times 100$$

and TU (toxic units) = 100/either the LC_{50}, EC_{50}, or ChV.

‡ % TR calculated only from individual pairs of influent and effluent samples (not the pooled data base)

sitive indicator of acute toxicity for the Patapsco wastewaters. The *C. dubia* mean 48-hr LC_{50} was 6.3% and the mean 7-day ChV was 2.5% effluent.

Except for most metals and eight organics, the Patapsco plant reduced influent priority pollutant concentrations to below the detection limit. The average effluent concentrations of 12 metals and 1 organic (alpha-hexachloro-cyclohexane) were found to exceed EPA water quality criteria for marine and freshwaters. In contrast to the chemical-specific data, results of the wastewater fractionation/identification tests indicated metals were not contributors to the plant's effluent toxicity

The evaluation of the two main influent sewers revealed that the wastewater entering the plant from the industrial service area was highly and consistently toxic as measured by the Microtox™ (EC_{50} about 3.5%). The influent wastewater from principally domestic-commercial contributors was highly toxic to Microtox™ (EC_{50} averaging about 7.6%) in the warm water seasons and moderately toxic (EC_{50} averaging about 21.6%) in the cool water season. The temperature dependence of the toxicity in the domestic-commercial wastewater suggested a warm weather septicity problem in the long sewers of the domestic-commercial collection area.

No significant correlations were found among Microtox™ EC_{50} values and the LC_{50} values of *C. dubia* and *M. bahia*. Microtox™ values exhibited strong correlations with wastewater characteristics and plant performance paramelers including suspended solids, BOD_5, and COD concentrations in the influent wastewater, and with increasing BOD_5 and COD concentrations in the secondary effluent. An overall analysis of the data, however, indicated that Microtox™ and the operations and performance parameters, including oxygen and COD uptake rates and ATP measurements, were not effective surrogates for the prediction of acute and chronic responses of *C. dubia* and *M. bahia*. Oxygen and COD uptake rates and ATP measurements were useful, however, in revealing inhibition effects on the Patapsco plant's biomass.

Characterization of Toxicity

Application of wastewater fractionation/identification procedures to primary effluent and secondary effluent Patapsco wastewaters provided perspective on the general characteristics of the toxic components producing toxicity at the Patapsco plant. The wastewater fractionation/identification procedures were able to characterize the broad classes of toxics responsible for the measured toxicity and to provide information on potential toxicity treatment options. GC/MS analysis of the toxic wastewater fractions, however, was not able to definitively identify the specific organic compounds causing the toxicity.

The wastewater fractionation procedure used a rapid screening test, *C. dubia* time lethality test, as the toxicity indicator to reveal (Figures 1 and 2) that non-polar (N-P) organic compounds were the principal toxicants in the influent and effluent wastewaters. Toxicity results for fractions of C_{18} methanol elution indicated that the N-P organic compounds causing toxicity have high log octanol to water partition coefficients and hence should adsorb onto solids. This observation was supported by a study that revealed the *C. dubia* toxicity in the Patapsco Plant effluent was largely associated with particles greater than 0.2 μm in size.

Lesser and intermittent amounts of wastewater toxicity were attributed to compounds removed by aeration and ammonia stripping. The presence of toxicity in the residual fraction of a secondary effluent sample (December 10, 1986) indicated that other compounds may contribute to effluent toxicity on an intermittent basis. This intermittent residual toxicity was most likely polar organic compounds not retained by the C_{18} column or non-polar organic compounds with molecular weights greater than 2000. The ion exchange separation procedures indicated that cations (metals) and anions were not principal causes of the effluent toxicity

Toxicity Source Evaluation

Using Microtox™ as the toxicity indicator, the batch treatability test revealed that only one of the five selected industrial wastewaters contained substantial toxicity that was refractory to treatment by the plant's biomass. The *C. dubia* test, however, indicated substantial levels of toxicity in the batch-treated effluents of all five industrial wastewaters. *C. dubia* tests on samples of plant biomass used for the batch tests revealed substantial toxicity in the filtrate (coarse filtration) of biomass. The biomass toxicity was associated with the solids passing the coarse filter, which was used to simulate plant clarification in the batch tests, and masked *C. dubia* measurements of refractory toxicity in the effluents from the batch treatability tests. Further studies revealed that most of the toxicity could be removed from the coarse filtrate by efficient filtration using a 0.2 μm pore size filter or by high speed centrifugation.

The combination of batch treatability and batch effluent fractionation procedures characterized the toxicity contribution by the individual industrial wastewater entering the central treatment plant (Table 2, Figures 3 and 4). The tests confirmed the importance of the N-P organics to the toxicity problem at the Patapsco plant. The batch treatability tests on the industrial wastewaters used ranges of concentrations of industrial wastewater greater than their influent concentration entering the central plant. The tests at the high concentrations of industrial wastewater revealed toxicity contributions from cations and anions in the batch test effluents that were not found in the effluent of the central treatment plant because of dilution by the overall plant

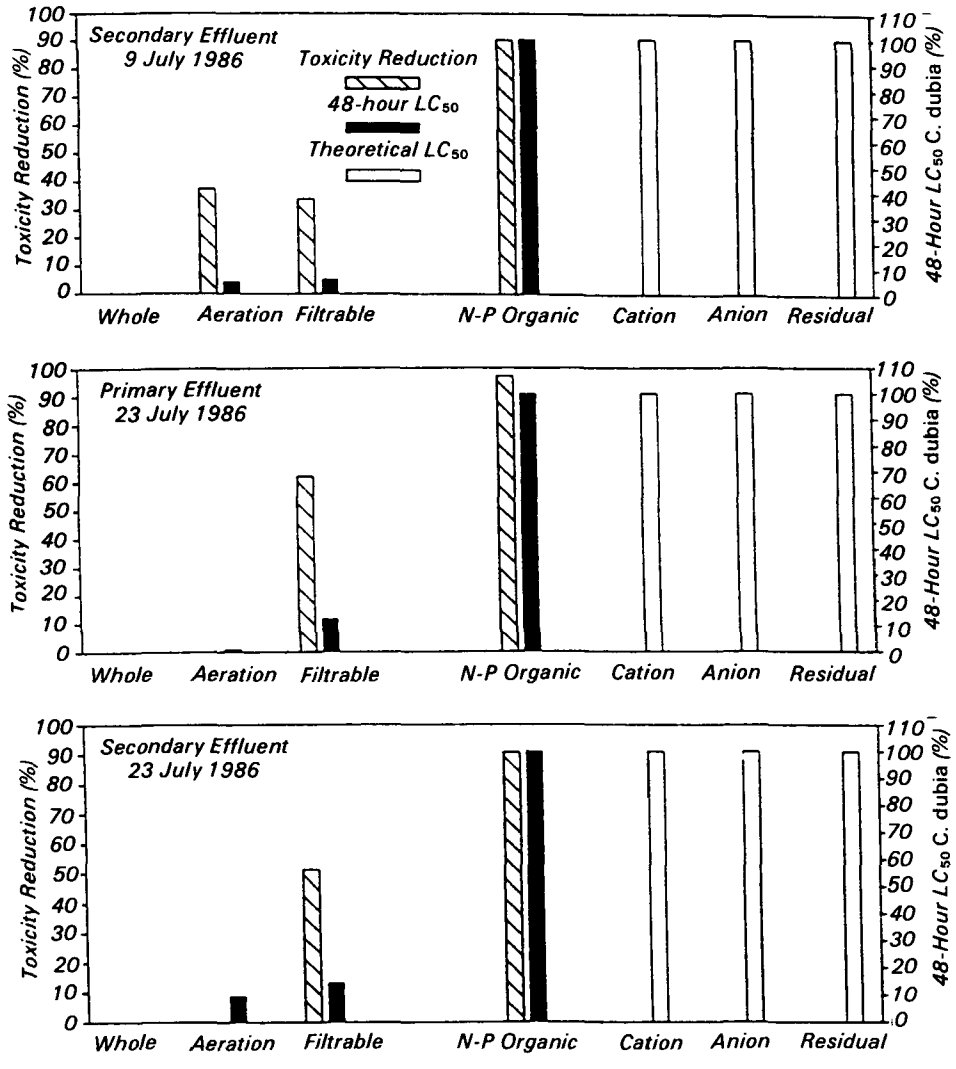

Figure 1. *Toxicity reduction and acute toxicity of various fractions of primary and secondary effluent samples from the Patapsco Plant, warm weather 1986.*

Table 2. *Principal Toxic Fractions of the Industrial Wastewater Discharges Refractory to Batch Treatment*

Industry	Sample Data	Principal Toxic Fraction*
A	December 12, 1986	Residual
	March 12, 1987	Non-Polar Organics
C	April 8, 1987	Non-Polar Organics
D	March 19, 1987	Non-Polar Organics
	April 15, 1987	Non-Polar Organics
E	March 26, 1987	Anions

*Based on the acute toxicity (C. dubia 48-hr LC_{50}) remaining after each fractionation step.

wastewater. Oxygen and COD uptake rate tests also characterized the industrial wastewater's potential for inhibition of the central plant's biomass

Conclusions

The conclusions of the TRE study at the Patapsco plant are as follows:

- The influent to the Patapsco plant e: hibited substantial acute and chronic to: icity as measured by *C dubia, M. bahi* and Microtox™ tests.
- Although a major reduction in toxicity wa achieved by the Patapsco plant, substa tial acute and chronic toxicity a measured by the *C. dubia, M. bahi* and Microtox™ tests was present in th plant effluent. The *C. dubia* test was th most sensitive indicator of acute toxici for the Patapsco plant's wastewaters an results of this test reveal a continuou discharge of effluent toxicity. The wat quality impacts of the Patapsco plant's e fluent toxicity on the Patapsco Riv estuary were not investigated and a thus unknown.
- The Patapsco plant performed well du ing the TRE period of May 1986, January 1987, and the pass-through toxicity was not caused by poor pla operation or performance. Based c historical Microtox™ data, the in plementation of secondary treatment an the gradual development of an a climated biomass in the secondary pr cess (1-yr) produced increases in toxic ty removal, and hence substantial redu tion in toxicity pass-through at th Patapsco plant.
- In-plant toxicity monitors (i.e., oxyge utilization, substrate utilization, and AT tests) were appropriate indicators of i hibitory effects on the Patapsco plant biomass. A comparison of results of i plant monitors and standard bioassa (i.e., 7-day *C. dubia*, 96-hr *M. bahia*, ar Microtox™ tests), however, found th these in-plant tests were not suitable su rogates for measurement of toxic effec on aquatic biota. Furthermore, the *dubia* and *M. bahia* tests were more se sitive indicators of effluent toxicity tha Microtox™.
- Historical Microtox™ data indicated th there was a significant increase in toxici following chlorination of the Patapsc secondary effluent. Because dechlorin tion will be implemented at the Patapsc plant in the near future, this toxici source was not evaluated during th TRE.
- Wastewater fractionation/identificati procedures were able to identify the bro classes of compounds responsible for th measured toxicity and to provide inf mation on potential toxicity treatme options. The wastewater fractionati procedure revealed that non-polar orgar compounds were the principal toxicar in both the influent and effluent wast waters. GC/MS analysis of the non-pol

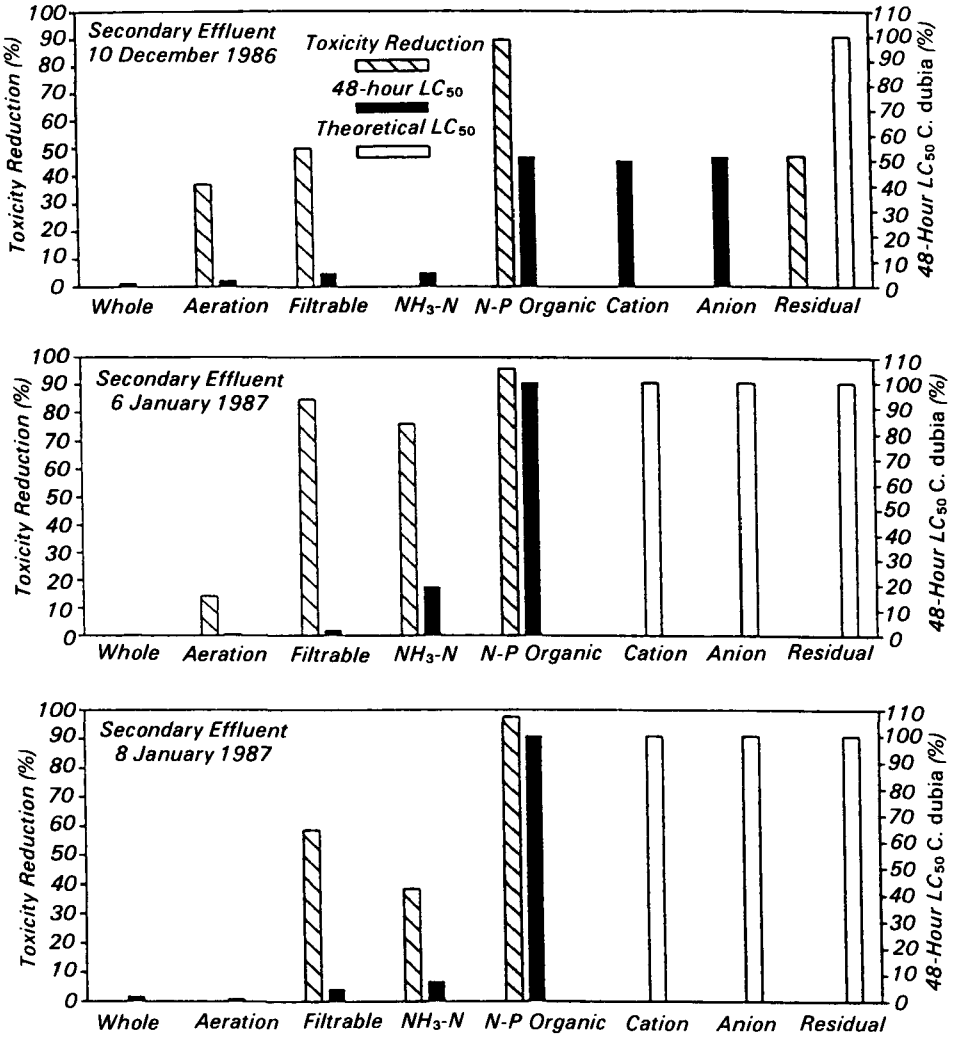

Figure 2. Toxicity reduction and acute toxicity of various fractions of secondary effluent samples from the Patapsco Plant, cool weather 1986.

organic fractions, however, was not able to identify the specific organic compounds causing the toxicity.

- Other results demonstrate that toxicity as measured by *C. dubia* was largely associated with particles greater than 0.2 μm in size. This observation is supported by the fractionation results, which indicated that the non-polar organic toxicants have relatively high log octanol to water partition coefficients and hence should adsorb onto solids. Based on the evidence of toxicity in the particulate phase of the effluent wastewater, enhanced solids removal at the Patapsco plant should provide an effective way to remove the major portion of the effluent toxicity.
- Lesser amounts of wastewater toxicity were attributed to compounds removed by aeration and ammonia fractionation treatment, and the occasional presence of toxicity in the residual fraction of some of the fractionation tests indicated that low levels of polar organic compounds may contribute to effluent toxicity on an intermittent basis. Wastewater fractionation/identification procedures revealed that metals were not a principal cause of the effluent toxicity.
- A toxicity treatability screening procedure was developed during the Patapsco TRE and was applied to five of the largest and most toxic industrial dischargers to the Patapsco plant. The toxicity treatability procedure was found to be an effective tool for identifying and ranking possible industrial contributors to the Patapsco plant's effluent toxicity. This procedure was also an effective tool for identifying industrial dischargers that interfere with biological treatment at the Patapsco plant; however, further research is needed to confirm that the data on interference effects are not false positive results.
- The combination of the toxicity treatability screening procedure and the fractionation procedure was an effective tool for tracking and for characterizing toxic influent wastewaters, which were refractory to treatment by the Patapsco plant's biomass.

The full report was submitted in fulfillment of Cooperative Agreement No. 812790-01-1 by the City of Baltimore under the sponsorship of the U.S. Environmental Protection Agency.

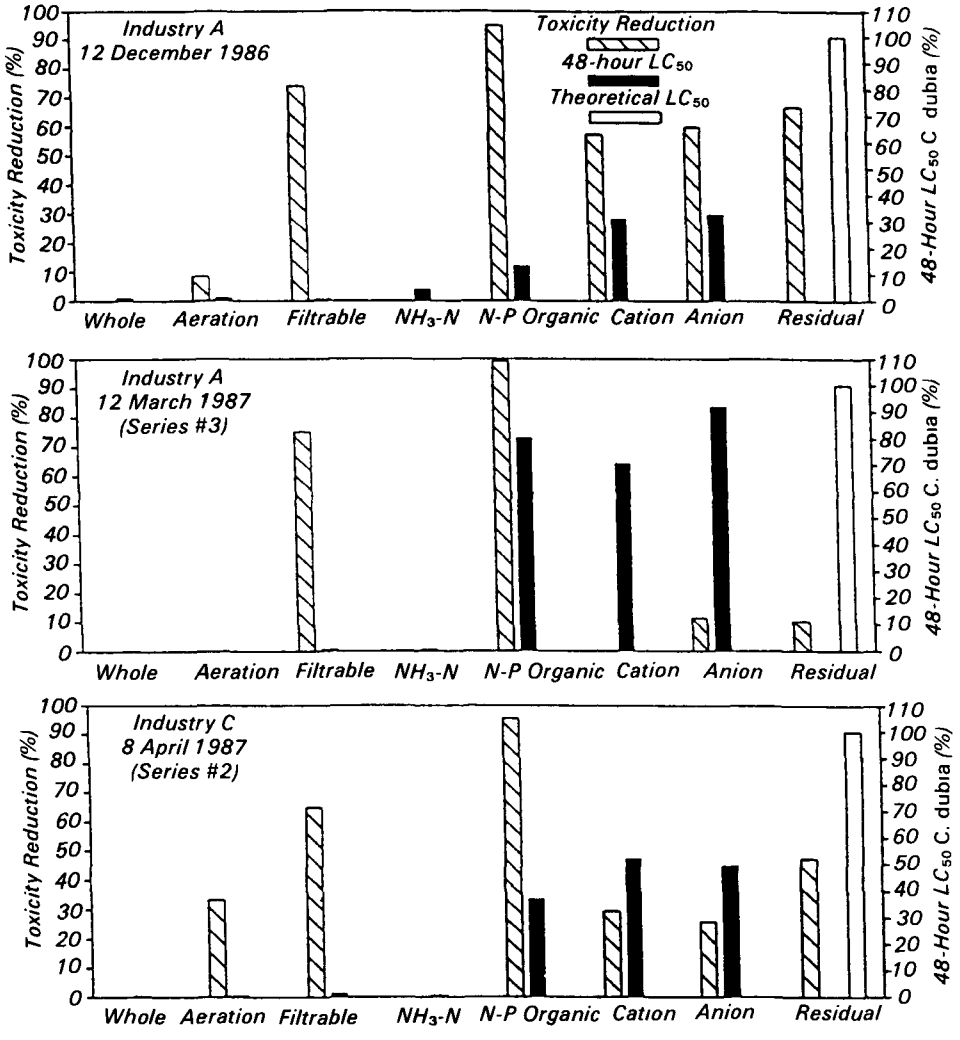

Figure 3. *Toxicity reduction and acute toxicity of various fractions of industrial wastewaters (A and C) from the toxicity treatability test.*

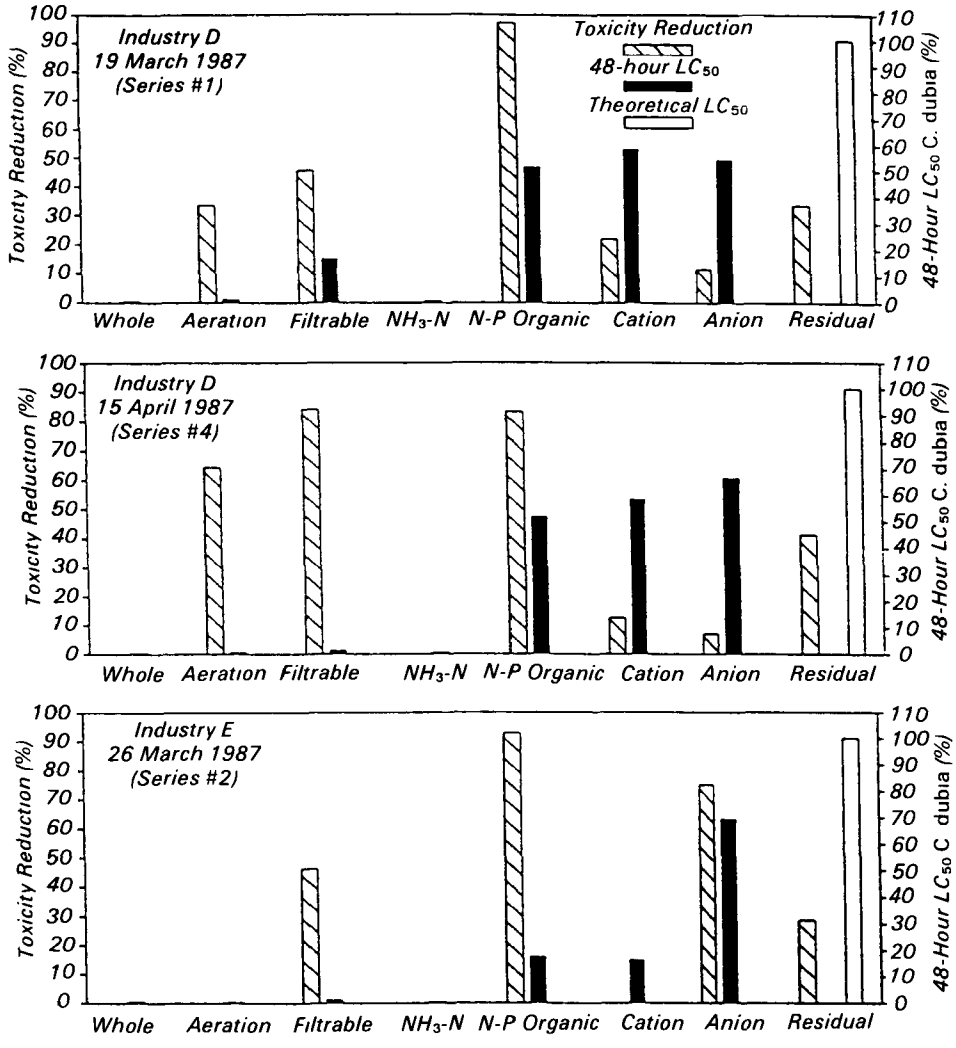

Figure 4. *Toxicity reduction and acute toxicity of various fractions of industrial wastewaters (D and E) from the toxicity treatability test.*

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The complete report, entitled "Toxicity Reduction Evaluation at the Patapsco Wastewater Treatment Plant," (Order No. PB 88-220 488/AS; Cost: $32.95, subject to change) will be available only from:

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