NOAA Technical Memorandum GLERL-123

DEGRADATION OF CHEMICAL BIOCIDES WITH APPLICATION TO BALLAST WATER TREATMENT

Peter F. Landrum[1], Larissa Sano[2], Mark A. Mapili[2], E. Garcia[2], Ann M. Krueger[2], and Russell A. Moll[3]

[1]NOAA, Great Lakes Environmental Research Laboratory, Ann Arbor, MI 48105
[2]Cooperative Institute for Limnology and Ecosystems Research, GLERL/Univ. of Michigan, Ann Arbor, MI
[3]Michigan Sea Grant, University of Michigan, Ann Arbor, MI

Great Lakes Environmental Research Laboratory
Ann Arbor, Michigan

June 2003

UNITED STATES
DEPARTMENT OF COMMERCE

Donald Evans
Secretary

NATIONAL OCEANIC AND
ATMOSPHERIC ADMINISTRATION

Conrad C. Lautenbacher, Jr.
Administrator

NOTICE

Mention of a commercial company or product does not constitute an endorsement by the NOAA. Use of information from this publication concerning proprietary products or the tests of such products for publicity or advertising purposes is not authorized. This is GLERL Contribution No. 1271.

This work was supported in part by grants from the Great Lakes Fishery Trust and the NOAA Ballast Water Technology Demonstration Program through the Cooperative Institute for Limnology and Ecosystems Research, University of Michigan and under cooperative agreement (NA67RJ0148) from the Office of Oceanic and Atmospheric Research, National Oceanic and Atmospheric Administration, U.S. Department of Commerce. Diversified Nutri-Agi Technologies, Inc., Gainesville, GA supplied the Disinfekt 1000® as a gift.

This publication is available as a PDF file and can be downloaded from GLERL's web site: www.glerl.noaa.gov. Hard copies can be requested from GLERL, Information Services, 2205 Commonwealth Blvd., Ann Arbor, MI 48105. pubs.glerl@noaa.gov.

Table of Contents

Figures

Tables

Degradation of Chemical Biocides with Application to Ballast Water Treatment

Peter F. Landrum, Larissa L. Sano, Mark A. Mapili, Elena Garcia, Ann M. Krueger, and Russell A. Moll

ABSTRACT. Biocide treatment of ballast tanks has been proposed as one possible method for reducing the number of nonindigenous species released into the Laurentian Great Lakes. One of the more widely cited drawbacks of biocide use is the potential for environmental effects to native organisms when the biocide is released into receiving waters. This report describes results from studies evaluating the degradation rates of three different biocides that could be used for treating the ballast water of transoceanic NOBOB (no ballast on board) vessels that trade on the Great Lakes. The three biocides tested were glutaraldehyde, Disinfekt 1000® (a glutaraldehyde-surfactant adjuvant mixture), and sodium hypochlorite (NaOCl). The data were collected as part of a larger study examining the efficacy of utilizing these biocides for ballast water treatment.

1. INTRODUCTION

The unintentional establishment of nonindigenous aquatic species through the release of ballast water has had a profound impact on aquatic ecosystems worldwide. This impact is particularly evident in the Laurentian Great Lakes, where the introduction of species such as the zebra mussel (*Dreissena polymorpha*) has affected populations of organisms (Schloesser et al. 1998, Nalepa et al. 2000) and altered important ecological processes (Klerks et al. 1997, Nicholls et al. 1999). The recent discovery of several new nonindigenous species (Dermott et al. 1998, Grigorovich and MacIsaac 1999, MacIsaac et al. 1999) demonstrates the urgent need for ballast water management in order to reduce the risk of future introductions.

In a 1996 report, the National Research Council (NRC 1996) identified a range of promising options for treating ballast water. Included in this list were chemical biocides (or 'biocides') that can be added to both ballasted and non-ballasted vessels in order to eliminate viable organisms. Biocide treatment is a potentially attractive option since it can be readily incorporated into both existing and future vessel designs and may be effective against a broad range of organisms (NRC 1996); however, the safety of such a treatment option may be limited by the degradation rate of the biocide and the potential release of biocidal concentrations into receiving waters. In addition, although biocides have been used extensively in certain industries for disinfection, the ballast tank environment is unique and may not be compatible with some biocides, which may react rapidly with organic material or may be corrosive at higher concentrations.

The objective of this study was to evaluate the degradation rates of three different biocides identified as potential candidates for ballast water treatment. The three compounds tested were glutaraldehyde (1,5-pentanedial, CAS Registry No. 111-30-8), glutaraldehyde plus a nonionic surfactant adjuvant (Disinfekt 1000®), and sodium hypochlorite. Glutaraldehyde is a potent microbial biocide and is widely used in several commercial and industrial applications including for sterilizing heat sensitive dental and medical equipment. Disinfekt 1000® (Diversified Nutri-Agri Technologies Inc., Gainesville, GA) is a combination of glutaraldehyde (20% v/v), a proprietary nonionic surfactant (~80% v/v), and methanol (~0.2% v/v), and is formulated for use in poultry hatcheries and farm animal housing facilities. Hypochlorite, a form of active chlorine, has been used as a disinfectant for many years and is particularly effective against bacteria and viruses.

The degradation experiments were designed to assess decay rates for biocide treatment of transoceanic NOBOB (no ballast on board) vessels that trade on the Great Lakes. These vessels are a potentially important vector for the release of viable nonindigenous species into the Great Lakes. Unlike ballasted vessels, NOBOBs do not engage in open-ocean exchange. Although technically unballasted, NOBOB vessels often carry up to several hundred tons of residual sediments and water in their tanks (Farley 1996). This material can harbor viable organisms and resting stages (Bailey et al. 2003) and thus constitute a major risk for the release of nonindigenous species (MacIsaac et al. 2002).

2. MATERIALS AND METHODS

2.1 Chemicals and Analytical Methods

2.1.1 Glutaraldehyde:

Glutaraldehyde was obtained as a 50% solution (w/w) in water from Fisher Scientific (Fairfield, NJ, USA). From this concentrated solution, a 0.1% stock solution was made in either filtered Huron River water (HRW) or filtered well water (WW). This stock was kept refrigerated at 4°C and was used for up to 4 weeks with no detectable decrease in glutaraldehyde concentration. Concentrations of glutaraldehyde were measured using a spectrophotometric assay with 3-methyl-2-benzothiazonlinone hydrazone hydrochloride as the color-developing agent (Sawicki et al. 1961; Pakulski and Benner 1992). The range of this method was 0.5 mg L^{-1}-8.0 mg L^{-1} of glutaraldehyde, and most test solutions had to be diluted in order to fall within the range of the analytical method. All concentrations are presented as mg glutaraldehyde L^{-1}.

2.1.2 Disinfekt-1000®:

The Disinfekt 1000®, was supplied by Diversified Nutri-Agri Technologies, Inc. (Gainesville, GA). Because the active ingredient in Disinfekt-1000® is glutaraldehyde, concentrations were measured using the same method employed for glutaraldehyde (described above). The results from standard addition experiments indicated no interference with the analytical method from the surfactant adjuvant.

2.1.3 Sodium Hypochlorite:

Purified grade sodium hypochlorite (4-6%) was obtained from Fisher Scientific (Fairfield, NJ, USA). Dilutions of the concentrated product were based on the estimate from the manufacturer that the solution contained 5.65% NaOCl. A 1% or 0.1% NaOCl stock solution was made by measuring the appropriate amount of 5.65% NaOCl and diluting with deionized water (DW), which is Ann Arbor (Michigan, USA) city water passed through a carbon filtration system and filtered through a Ropure® ST reverse osmosis system (Barnstead, Dubuque, IA, USA) and a Nanopure® UV ultrapure water system (Barnstead, Dubuque, IA, USA). Stock solutions were kept at 4°C in the dark. Prior to each use, the chlorine concentration was measured for a 2 mg L^{-1} solution made from the stock to assure the integrity of the solution. If the chlorine measurement dropped below 1.70 mg L^{-1}, the stock solution was discarded and a fresh one made.

Chlorine content in mg L^{-1} was measured using the VVR Water Analysis System from CHEMetrics, Inc. (Calverton, VA, USA). This photometric method measures the color intensity of N, N-diethyl-p-phenylenediamine when oxidized by free chlorine. To measure total chlorine, potassium iodide was added to the sample prior to the measurement. Because the system measures chlorine in the range of 0-6 mg L^{-1}, it was sometimes necessary to dilute samples with DW prior to measurement. The spectrophotometer was zeroed using the water that comprised the majority of the sample, either DW, filtered well water (WW), or filtered Huron River water (HRW: see experimental protocol below). If turbidity was present, the sample was centrifuged for 5 minutes at setting of 100 on a DYNAC centrifuge (Parsipanny, NJ, USA) prior to chlorine measurement.

2.2 Degradation Experiments

2.2.1 Water Sources:

Water for the degradation experiments came from two different sources: Huron River water (HRW) was collected from on upstream site on the Huron River at the Hudson Mills Metropark near Dexer, MI. The HRW had a total hardness of 165 mg L^{-1} as $CaCO_3$, total alkalinity of 3.996 meq L^{-1}, and a pH range of 8.2-8.6. Well water (WW) was collected from a ground well located at the United States Geological Survey, Great Lakes Science Center (Ann Arbor, MI). It had a total hardness of 500 mg L^{-1} as $CaCO_3$,a total alkalinity of 5.00 meq L^{-1} and a pH range of 7.2-7.8.

2.2.2 Glutaraldehyde:

Two groups of degradation experiments were performed using glutaraldehyde: preliminary degradation experiments to assess whether decay was affected by the presence of bacteria and more comprehensive biodegradation experiments utilizing different exposure media to assess decay rates.

To evaluate the effect of microbial activity on glutaraldehyde degradation rates, a preliminary experiment using secondary sewage sludge was conducted at two temperatures, 4°C and 25°C. Experiments were conducted in HRW, which had been filtered through a Cole Palmer prefilter (Vernon Hills, IL, USA) and a 3.0 μm Millipore filter (Bedford, MA, USA). Treatments were inoculated with 0.5 mL of secondary sewage sludge collected from the Ann Arbor wastewater treatment facility (Ann Arbor, MI, USA). The controls consisted of the same water as the treatments, but were not inoculated with sludge. Experiments were maintained in the dark at either 25°C or 4°C, and samples were collected approximately every 48 h.

Another preliminary experiment was conducted to measure changes in bacteria density associated with glutaraldehyde degradation. Huron River water was filtered through a 3.0 mm Millipore filter (Bedford, MA, USA) and allowed to equilibrate in sterile containers at 25°C for 24 hours to allow the bacterial population to stabilize. For each test concentration, a sterile solution was made to assess non-bioloigcal degradation. Huron River water was filter sterilized through an autoclaved 0.2 μm Micronics® filter (Redmond, Washington). All instruments used for bioassay were autoclaved (sterilized) prior to use. Using the equilibrated HRW, a toxicant dilution series was prepared, including controls. Initial measurements of temperature, glutaraldehyde concentration, and bacterial density were made prior to initiation of the experiment. Bacteria counts were made using epifluorescence microscopy and the stain 4',6-diamidino-2-phenylindole (DAPI), which complexes with DNA and permits a direct total cell count of bacteria (Porter and Feig 1980). This stock solution of DAPI was made in filtered distilled, deionized water. For bacterial counts, the samples of bacteria (plus DAPI stain) were filtered through a 0.2 μm Anodisc filter (Whatman, Inc., Clifton, NJ, USA). The samples were then destained with 1 mL of 25% isopropanol for a total contact time of 2.5-3 min. The filter was placed on a microscope and low-fluorescing immersion oil was added. Counts were made with a 100x Leitz lens and at least 400 cells were counted to improve statistical determination of density. Cell counts were then converted to cell mL^{-1} based on the number of fields per filter and the test volume of the sample.

The protocol for the second set of biodegradation experiments was adapted from ASTM (1998). Experiments were conducted in 250 mL Erlenmeyer flasks. Four concentrations of glutaraldehyde were evaluated (0 mg L^{-1}, 10 mg L^{-1}, 100 mg L^{-1}, 500 mg L^{-1}), and the ratio of water-sediment was 8:1 (v/v). The total vessel volume (sediment plus water) was 100 mL. The sediment used for these experiments was collected from the Geddes Pond in Gallup Park (Ann Arbor, MI). Sediments were taken from shallow water (approximately 4-6 inches in depth) at a site located adjacent to the shoreline. The organic carbon content of the sediment was determined after removing carbonates with 1 N HCL, re-drying the sample, and measuring carbon on a CE Instruments 1110 CHN analyzer (ThermoQuest, Italia, Milan, Italy). Organic carbon content of these sediments averaged 2.6 ± 0.4%. Sediments were used within 48 hours of collection, and prior to use, the sediments were sieved through a 1.2 μm mesh and homogenized thoroughly. The water used for the experiments was HRW.

Degradation rates were assessed under four different exposure conditions: (1) natural water-only (NW) using unfiltered HRW (Huron River water); (2) natural water-sediment (NWS) using unfiltered HRW and untreated sediments; (3) sterile water-only (SW) using filter-sterilized HRW; and (4) sterile water-sediment (SWS) using filter sterilized HRW and steam sterilized sediments. The sterile HRW used in the experiments was sterilized using an autoclaved 0.20 μm filter (Micronics, Inc., Redmond, Washington). Sediments were sterilized by placing them in an autoclave and heating to 120°C for 22-25 minutes.

Experiments employing glutaraldehyde were maintained in the dark and conducted at three different temperatures (5°C, 15°C, and 25°C). Flasks were placed on an orbital shaker set at 100 rotations per minute (rpm) to mimic the mixing that might occur in transoceanic NOBOBs. Water samples were collected approximately every 48 hours for glutaraldehyde determination, and the experiments were maintained for 28 days.

2.2.3 Disinfekt 1000®:

A 28-day degradation experiment was performed using Disinfekt 1000®. Four concentrations of Disinfekt 1000® were used (where the concentration is expressed as active glutaraldehyde): 0 mg L^{-1}, 10 mg L^{-1}, 100 mg L^{-1}, and 500 mg L^{-1}. These concentrations were used under four different test conditions: (1) natural water-only (NW), in which solutions were prepared using prefiltered HRW (prefiltered with a Cole Palmer submicrofilter (Vernon Hills, IL, USA)); (2) sterile water-only (SW), in which solutions were prepared using 0.22 μm filter-sterilized HRW; (3) natural water-sediment (NWS), in which solutions were prepared using prefiltered HRW, and Geddes Pond sediment in a 4:1 water-sediment ratio (v/v); (4) sterile water-sediment (SWS), in which solutions were prepared using 0.22 μm filter-sterilized HRW and combined with sterilized (autoclaved) Geddes Pond sediment in a 4:1 water-sediment ratio (v/v).

Test concentrations, including controls, were prepared in duplicate using 250 mL Erlenmeyer flasks as test vessels. Total vessel volume was 100 mL. Test vessels were kept in the dark and maintained at 25°C for 28 days. Initially, the test vessels were sampled every day for 3 days, then every 2-5 days for the remainder of the test.

2.2.4 Sodium Hypochlorite:

Two degradation experiments were conducted using hypochlorite. The first experiment consisted of monitoring chlorine content in filtered WW and filtered HRW under low intensity (20 lux), gold fluorescent light (l>500 nm). The WW was filtered through 0.45 and 0.22 μm Millipore filters (Bedford, MA, USA). The HRW was prefiltered using a 0.22 mm mesh and then filtered through a 0.45 μm and 0.22 μm Millipore filter. Two 300 mL beakers were filled with 200 mL of a 2 mg L^{-1} chlorine solution made with filtered WW, and two 300 mL beakers were filled with 200 mL of the 2 mg L^{-1} chlorine made with filtered HRW. After solution addition, the four test beakers were left uncovered for 20.5 minutes. Measurements of free chlorine in one of the duplicates were taken at 0, 2.5, 5, 7.5, 10, 15, and 20 minutes, while the other duplicate was measured for chlorine 0.5 minutes after the first one. Each sample required a 15-20 mL aliquot of solution.

A second degradation experiment was conducted to assess decay rates in three different media: sterilized DW, unfiltered HRW, and unfiltered HRW with sediments (in a 8:1 water:sediment ratio (v/v)). The sediments were collected from Geddes Pond (described above). Ten replicates each of a 10, 100, and 500 mg L^{-1} hypochlorite concentration were made using the three different media. Chlorine solutions added to the water-sediment treatments were increased to adjust for sediment dilution. Test chambers consisted of 125 mL Erlenmeyer flasks, and contained a total volume of 100 mL. After addition of solution and sediments, flasks were sealed with aluminum foil, placed on an orbital shaker at 66 rpm, and held in the dark at 16°C. Total chlorine measurements were taken at 2, 6, 24, 48, and 96 h from two replicates at each hypochlorite concentration and water type. Flasks were sampled destructively and at the end of 96 h, DO and pH were recorded in the remaining flasks.

2.3 Data Analysis

Degradation data were analyzed primarily using regression analysis in SYSTAT Version 10 (SPSS, Inc., Chicago, IL). When the estimated measured concentration was lower than the analytical detection limit, the estimate was assigned a value of zero and the regression model calculated based on this correction. In addition, samples from the controls for some of the water-sediment samples (primarily sterile water-sediment exposures using glutaraldehyde) registered significant background concentrations using the MBTH analysis, with concentrations in the 1 mg glutaraldehyde L^{-1} range. To correct for this, the background values from the spectrophotometer readings were corrected for dilution and subtracted from the spectrophotometer readings for the 10 mg L^{-1} water-sediment samples for the glutaraldehyde degradation experiments. The level of interference in the other experiments was negligible and did not warrant correction. Comparisons of regression models were made using indicator variables generated from general regression models in SYSTAT. Half-life estimates were based on the slope of the line (k) for log transformed data and assumed a first-order decay rate.

3. RESULTS

3.1 Glutaraldehyde

3.1.1 Preliminary biodegradation experiments:

Data indicated that glutaraldehyde degradation rates vary as a function of bacteria biomass. The addition of sludge drastically increased the degradation rate of glutaraldehyde at 25°C (Figure 1). The first-order half life for the 25 mg L^{-1} glutaraldehyde treatment with sludge was 34 h compared to a half-life of 1500 h for the water-only (no sludge) exposure. Similarly, at a concentration of 5 mg L^{-1} of glutaraldehyde, the half-life of the treatment with sludge was substantially shorter (48 h versus 107 h without sludge addition). In contrast, minimal degradation occurred at 4°C, even with sludge addition. These experimental findings indicate both that the addition of bacteria can enhance glutaraldehyde degradation and that the degradation rate is temperature dependent. Data from experiments using the DAPI stain indicated that changes (increases) in bacteria density were associated with decreasing glutaraldehyde concentrations. Data from the 17 mg L^{-1} glutaraldehyde treatment are provided in Figure 2. At 25°C, glutaraldehyde degradation was detectable at 120 hours. This decrease was associated with a concomitant increase in the number of bacteria.

3.1.2 5° degradation:

The degradation rate of glutaraldehyde at 5°C varied with exposure conditions and only the water-sediment exposures demonstrated statistically significant degradation rates (i.e., k>0; Table 1). The slopes of the regression lines were significant for the 10 mg L^{-1} and 100 mg L^{-1} treatments for both the natural and sterile water-sediment exposures (Figures 3 and 4). Based on the slope of the lines, the degradation rate was highest for the 10 mg L^{-1} treatment in the natural water-sediment exposure (slope (k) = -4.167×10^{-3} h^{-1}). The half-life at 5°C ranged from 171 hours to greater than 15,000 hrs (600 days: Table 2). Only the 10 mg L^{-1} concentration for the natural water-sediment exposure and sterile water-sediment exposure had half-life values of less than 30 days (7 days and 20 days, respectively).

A comparison of regression lines indicated no statistical difference in the degradation rates between sterile and natural water-only exposures for all concentrations tested (p=0.9 for 10 mg L^{-1}, p=0.07 for 100 mg L^{-1}, p=0.7 for 500 mg L^{-1}). The results were similar for natural and sterile water-sediment treatments, except that at 10 mg L^{-1} the slopes of the lines were different (p=0.005).

The degradation rates of some of the treatments were characterized by a lag phase (or adaptation phase). In particular, the 10 mg/L treatments in natural water-sediment exposures demonstrated a lag phase, in which minimal degradation occurred followed by a rapid increase in the degradation rate. For the 5°C experiment, this lag phase lasted for approximately 340 hours.

3.1.3 15° degradation:

At 15°C, degradation rates also varied by exposure conditions. In contrast to results at 5°C, all of the treatments in the water-sediment exposures at 15°C had statistically significant degradation in addition to the 10 mg L^{-1} treatments for both the natural and sterile water-only exposures (Figures 5-8). The degradation rate was greatest for the 10 mg L^{-1} natural water-sediment exposure (k=-1.224×10^{-2} h^{-1}: Table 1). The treatment with the second highest degradation rate was the 10 mg L^{-1} sterile water-sediment exposure (k=-1.39×10^{-2} h^{-1}). Half-life values at 15°C ranged from 35 hours to 9849 hours (Table 2). The shortest half-lifes were for 10 mg L^{-1} in natural water-sediment ($t_{1/2}$ = 35 hrs), 10 mg L^{-1} in sterile water-sediment ($t_{1/2}$ = 50 hrs) and 100 mg L^{-1} in natural water-sediment ($t_{1/2}$ = 350 hrs). The half-life values for the water-sediment exposures were significantly lower than for the water-only exposures.

Results from the 15°C degradation experiments also indicated no significant difference between the slope of the line for natural and sterile water-only exposures. The probability estimates for 10 mg L^{-1}, 100 mg L^{-1}, and 500 mg L^{-1} were p=0.99, p=0.42, and p=0.44, respectively. For the water-sediment treatments, the regression slopes

Table 1. Degradation data for glutaraldehyde experiments. Abbreviations are as follows: NW = natural water only, NWS = natural water-sediment exposure, SW = sterile water-only, SWS = sterile water-sediment exposure. Values italicized and in bold indicate a significant p value (<0.05).

				5°C			
		NW				**NWS**	
	10 mg/L	100 mg/L	500 mg/L		10 mg/L	100 mg/L	500 mg/L
slope (k)	-2.853E-04	2.034E-04	1.636E-04		-4.062E-03	-5.772E-04	-1.359E-04
p (k=0)	0.376	0.061	0.144		0.001	0.005	0.393
mutliple R^2	0.088	0.319	0.222		0.7665	0.608	0.082
		SW				**SWS**	
	10 mg/L	100 mg/L	500 mg/L		10 mg/L	100 mg/L	500 mg/L
slope (k)	-4.569E-05	2.949E-04	1.392E-04		-1.466E-03	-3.425E-04	3.802E-05
p (k=0)	0.895	0.097	0.409		0.000	0.045	0.845
mutliple R^2	0.002	0.276	0.077		0.777	0.375	0.004
				15°C			
		NW				**NWS**	
	10 mg/L	100 mg/L	500 mg/L		10 mg/L	100 mg/L	500 mg/L
slope (k)	-1.478E-03	-1.603E-04	-1.286E-04		-2.001E-02	-1.977E-03	-6.875E-04
p (k=0)	0.001	0.325	0.361		0.009	0.000	0.002
mutliple R^2	0.637	0.088	0.076		0.852	0.84	0.597
		SW				**SWS**	
	10 mg/L	100 mg/L	500 mg/L		10 mg/L	100 mg/L	500 mg/L
slope (k)	-8.911E-04	-1.439E-04	-7.036E-05		-1.388E-02	-1.021E-03	-5.761E-04
p (k=0)	0.008	0.39	0.595		0.002	0.000	0.000
mutliple R^2	0.492	0.068	0.027		0.925	0.865	0.86
				25°C			
		NW				**NWS**	
	10 mg/L	100 mg/L	500 mg/L		10 mg/L	100 mg/L	500 mg/L
slope (k)	1.551E-03	-1.879E-04	-3.023E-04		-2.981E-02	-6.534E-03	-1.055E-03
p (k=0)	0.014	0.022	0.011		0.000	0.000	0.000
mutliple R^2	0.5534	0.5005	0.5785		1	0.959	0.8582
		SW				**SWS**	
	10 mg/L	100 mg/L	500 mg/L		10 mg/L	100 mg/L	500 mg/L

		5°C	
	10 mg/L	100 mg/L	500 mg/L
NW	2429	N/A	N/A
NWS	171	1201	5100
SW	15167	N/A	N/A
SWS	473	2023	N/A
		15°C	
	10 mg/L	100 mg/L	500 mg/L
NW	469	4324	5391
NWS	35	350	1008
SW	778	4816	9849
SWS	50	679	1203
		25°C - exp #1	
	10 mg/L	100 mg/L	500 mg/L
NW	447	3688	2293
NWS	23	106	657
SW	172	N/A	18132
SWS	339	424	1109
		25°C - exp #2	
	10 mg/L	100 mg/L	500 mg/L
NW	256	3647	1873
NWS	35	93	578
SW	401	3300	2166
SWS	127	396	648

Table 2. Half-life estimates for glutaraldehyde degradation. Values are provided in hours. Abbreviations are as follows: NW = natural water only, NWS = natural water-sediment exposure, SW = sterile water-only, SWS = sterile water-sediment exposure. N/A indicates that data are not available (for these situations, the slopes of the lines were positive and did not yield a half-life estimate).

were the same at 10 mg L^{-1} and 500 mg L^{-1} ($p=0.514$ and $p=0.5514$, respectively), but the regressions at 100 mg L^{-1} did differ significantly ($p=0.003$).

For the 15°C experiment, there was evidence of a lag (or adaptation phase) that lasted for approximately 70 hours. The only treatment with a prominent adaptation phase was the 10 mg L^{-1} treatments in natural water-sediment exposures.

3.1.4 25° degradation:

Two independent experiments were conducted at 25°C. In the first experiment, glutaraldehyde degradation was significant in 9 out of the 12 different treatments (Table 1: Figures 9-12). The only treatments that did not demonstrate significant degradation were the 100 mg L^{-1} and 500 mg L^{-1} sterile water-only and the 10 mg L^{-1} sterile water-sediment exposures. The fastest degradation rate occurred in the natural water-sediment environment at 10 mg $^{-1}$L ($k=-2.980 \times 10^{-2}$ h^{-1}). The second fastest degradation rate also occurred in the natural water-sediment treatments, but at 100 mg L^{-1} glutaraldehyde ($k=-6.534 \times 10^{-3}$ h^{-1}). Based on these values, the degradation rate at 10 mg/L was almost 5 times faster than degradation at 100 mg L^{-1} glutaraldehyde. The half-life values (Table 2) follow the trends in the slope values. The shortest half-life (of 23 hours) occurred with the 10 mg L^{-1} natural water-sediment treatment. For this experiment, even the 10 mg L^{-1} sterile water-only treatment had a half-life of 173 hours (7 days). This rapid rate of degradation in a sterile environment might be due either to abiotic processes or to bacteria contamination of the test vessels.

For the second experiment, the only treatment that did not demonstrate a significant degradation constant was the 100 mg L^{-1} treatment in sterile water (data not shown). Overall, the results for the second experiment were similar to those from the first as demonstrated by the half-life estimates (Table 2). The only significant differences were with the sterile water-only and sterile water-sediment treatments: The half-life values for the second experiment were generally lower than the estimates from the first experiment, most notably for the 10 mg L^{-1} SWS and the 500 mg L^{-1} SW treatments.

Unlike the other two treatment temperatures, none of the treatments held at 25°C demonstrated a significant lag phase within the sampling regimen. Most of the decay rates were characterized by a relatively continuous decline in glutaraldehyde. The main exception was the 10 mg L^{-1} natural water-sediment exposure. For the first experiment, complete degradation of glutaraldehyde occurred in this treatment between the start time and the next sampling period (80 h).

3.1.5 Temperature comparisons:

Results from degradation studies indicate that low concentrations of glutaraldehyde degrade most rapidly in a water-sediment environment. Only minimal degradation occurred in water-only exposures over the 28-day period, except for most of the treatments held at 25°C.

There was a statistically significant difference in the slopes of the lines for the 10 mg L^{-1} and 100 mg L^{-1} natural water-sediment exposures at all three temperatures tested. Degradation rates in the natural water-sediment exposures increased with temperature: rates at 25°C were higher than those at 15°C, which were higher than those at 5°C.

3.2 Disinfekt-1000®

Degradation of glutaraldehyde in Disinfekt 1000, occurred in both the water-only and water-sediment exposures (Figures 13-16). Generally, degradation was observed to be greatest in the 10 mg L^{-1} water-sediment treatments (Table 3). Moreover, degradation was greater in natural water-sediment exposures over the 28 d period. In the presence of sediment, the half-life of glutaraldehyde at 10 mg L^{-1} was 120 hours (5 days) for non-sterile sediment, and 240 hours (10 days) for sterile sediment (Table 4). In water-only exposures, the half-life of glutaraldehyde was approximately 360 hours (15 days) in both sterile and non-sterile conditions. Sterile, water-sediment vessels at 100 mg L^{-1} were damaged shortly after the initiation of the test, and degradation data were not obtained from this treatment.

Table 3. Degradation data for Disinfekt 1000®. Abbreviations are as follows: NW = natural water only, NWS = natural water-sediment exposure, SW = sterile water-only, SWS = sterile water-sediment exposure. Values italicized and in bold indicate a significant p value (<0.05).

				25°C			
		NW				NWS	
	10 mg/L	100 mg/L	500 mg/L		10 mg/L	100 mg/L	500 mg/L
slope (k)	-1.860E-03	-2.700E-04	-5.500E-04		-4.097E-02	-6.900E-03	-9.600E-04
p (k=0)	0.00029	0.00272	0.00126		0.09737	0.00015	0.00008
mutliple R^2	0.78451	0.65015	0.70313		0.97679	0.84997	0.83842
		SW				SWS	
	10 mg/L	100 mg/L	500 mg/L		10 mg/L	100 mg/L	500 mg/L
slope (k)	-1.980E-03	-3.700E-04	-5.800E-04		-3.000E-03	N/A	-8.900E-04
p (k=0)	0.00032	0.00032	0.00137		0.00327	N/A	0.00039
mutliple R^2	0.77849	0.77871	0.69783		0.63606	N/A	0.76937

		25°C	
	10 mg/L	100 mg/L	500 mg/L
NW	365	2310	1386
NWS	33	100	693
SW	347	1733	1155
SWS	103	N/A	770

Table 4. Half-life estimates for Disinfekt 1000® degradation. Values are provided in hours. Abbreviations are as follows: NW = natural water only, NWS = natural water-sediment exposure, SW = sterile water-only, SWS.

3.3 Sodium Hypochlorite

Results from the first degradation experiment in sterilized water indicated that free chlorine degraded more quickly in filtered HRW compared to filtered WW over a 20.5 min time period (Figure 17). After solution preparation, initial measurements of free chlorine in filtered water were 87% of nominal values in WW and in filtered HRW were 52% of nominal value. The half-life of free chlorine in filtered WW was 81.5 minutes, while in filtered HRW it was 13.3 minutes. This is likely due to the reaction of chlorine with dissolved organic matter in the HRW, since both water samples had been filter-sterilized.

The second degradation study provided a better indication of the fate of the disinfectant after initial decay in a ballast tank. The results suggest that degradation rates depend on both the initial hypochlorite concentration and the composition of the exposure media (Figures 18-20). After the first sampling period (at 2 h), the total chlorine concentration in the sterile, deionized water was 86.2%, 88.1%, and 85.6% of the nominal concentration for the 10, 100, and 500 mg L^{-1} concentrations, respectively. After 2 h, solutions made with unfiltered HRW were 46.3%, 39.7%, and 86.8% of the nominal concentration for the 10, 100, and 500 m L^{-1} concentrations, respectively. Solutions made using unfiltered HRW and containing 11% sediment, showed a dramatic drop in total chlorine levels after 2 h at 2.4%, 0.5%, and 54% of the nominal concentrations for the 10, 100, and 500 nominal concentrations, respectively. The half-life values for total chlorine of the 10, 100, and 500 mg L^{-1} solutions after initial degradation were 693, 385, and 1,733 h (respectively) using deionized water, while the reported values using unfiltered HRW were 23, 224, and 533 h (respectively). Using unfiltered HRW containing 11% sediment, the half-life values after the initial decay were 25, 44, and 13 h, respectively.

4. DISCUSSION

Data from the glutaraldehyde experiments suggest that short-term decay may be largely determined by bacteria concentrations. Experiments using bacterial counts indicate increasing bacterial concentrations that coincide with decreasing glutaraldehyde concentrations. Further, the addition of secondary sewage sludge (which contains large numbers of bacteria and other microorganisms) resulted in a more rapid decay rate at the higher temperature tested (25°C). This rate increase was not present at 4°C, indicating that perhaps bacterial (or microorganism) production at this low temperature was retarded.

Results from degradation experiments at three temperatures and using four different treatments demonstrated that degradation rates were temperature dependent, and that the presence of sediments dramatically increased degradation rates (at lower glutaraldehyde concentrations). At 5°C, the only significant degradation occurred in water-sediment exposures. Both the natural and sterile water-sediment environments had significant glutaraldehyde degradation; however, the degradation rate was substantially higher in the natural water-sediment treatments. Similarly, at 15°C, all of the water-sediment exposures had statistically significant degradation rates. Further, both the natural water-only and sterile water-only treatments demonstrated significant degradation rates. Similar to the results at 5°C, the degradation rates were faster in the natural water-sediment exposures. Finally, at 25°C all of the treatments except three demonstrated significant degradation rates. Surprisingly, one of the treatments that did not have a significant degradation rate was the sterile water-sediment treatment at 10 mg L^{-1} glutaraldehyde. This appears to be an anomaly, since both the 100 mg L^{-1} and 500 mg L^{-1} had significant slopes, and the 10 mg L^{-1} sterile water-sediment exposure at both 5°C and 15°C had significant slopes. The half-life for the 10 mg L^{-1} natural water-sediment treatment was 23 hours. This value is similar to the estimated half-life for the 25 mg L^{-1} treatment with sludge conducted in the preliminary studies (34 h half-life for the sludge treatment versus 23 h half life for the water-sediment exposure).

These data indicate that bacteria likely play an important role in glutaraldehyde degradation. This inference is supported by Leung (2001a), in which rapid glutaraldehyde degradation rates were associated with bacteria activity in both water and sediments. The test concentration utilized in this set of experiments was 9.5 mg L^{-1} and although bacterial activity initially decreased after glutaraldehyde addition, it rapidly rebounded and increased over the course of a 31-day exposure. Bacterial activity was approximately 50 times greater in the sediment than in the

water column. The reported first-order half-life of decay was 10.6 h at 25°C. In addition, Leung (2001a) reported minimal degradation of glutaraldehyde under sterile conditions at a pH of 5 and 7. Degradation of the parent compound under sterile conditions and over the 31-day period was approximately 5% at a pH of 5 and 21% at a pH of 7. In comparison, at a pH of approximately 8.5, the 10 mg L^{-1} solution had degraded 76%.

Results from this study also documented degradation in sterile water-sediment treatments maintained at 15°C and 25°C. Leung (2001a) reported that under sterile conditions, degradation was pH-dependent. At pH values of 5 and 7, degradation was minimal, while at a pH of 9 degradation was appreciable (with a half-life of 46 days (1100 hours) at a concentration of 9.5 mg L^{-1} glutaraldehyde). In comparison, the half-life estimate from these experiments for the 10 mg L^{-1} sterile water-only treatment (at 25°C) was 172 h (or 401 h for the second experiment). This discrepancy in half-life values may be due to the presence of bacteria in the test vessels, either from incomplete sterilization of the sediment and/or water, or from subsequent contamination during sample collection. If the source of contamination was from incomplete sterilization of test vessels, this has an important implication for ballast water treatment. One proposed management option is to heat incoming ballast water to high temperatures to eliminate viable organisms. If thermophilic bacteria were able to persist in these sterilized test flasks, then there is a high probability that similar bacteria would survive in ballast water treated with heat. Regardless of the role of the bacteria, the results from Leung (2001a) indicate that glutaraldehyde will degrade abiotically, particularly at higher pH values. The high pH found in the Great Lakes (pH > 8) should therefore further facilitate the degradation of any residual biocide discharged into these receiving waters and thereby reduce possible environmental impacts.

In terms of the water-sediment exposures, it is likely that some percentage of the glutaraldehyde partitioned to the sediments. Although glutaraldehyde has a low K_{oc} value (Leung 2001b) and thus leaches readily from sediments, it was also found to distribute to sediments from water (Leung 2001a). The reported percent of glutaraldehyde in a water-sediment exposure varied from 94% in water and 9% in sediment at 4 h, to 50% in water and 25% in sediment after 2 days (see Leung 2001a). Thus, partitioning may explain, in part, the decrease in glutaraldehyde concentration in the sterile water-sediment exposures reported from these experiments.

These results suggest that higher concentrations of glutaraldehyde (100 mg L^{-1} and 500 mg L^{-1}) may be sustained in a ballast tank environment for a substantial amount of time. Even at 25°C, the estimated half-life of 500 mg L^{-1} in a natural water-sediment environment is 657 h (or approximately 27 days). For the natural water-sediment environment at 100 mg L^{-1}, the estimated half-life is 106 h (or 4.4 days). At the other end of the spectrum, lower concentrations of glutaraldehyde (e.g., 10 mg L^{-1}) will likely degrade relatively rapidly at both 15°C and 25°C under natural water-sediment conditions (half-life of 35 hours and 23 hours, respectively). This rapid decay rate should reduce the amount of glutaraldehyde released into receiving water after reballasting of NOBOB vessels. In addition, the amount of glutaraldehyde actually released will likely be much lower than the concentrations tested, due to dilution, diffusion, and dispersion of the released water.

Experimental results using Disinfekt 1000®, indicate that glutaraldehyde in this formulation degrades in both water-only and water-sediment environments. A higher rate of degradation occurred at lower concentrations and in the presence of sediment. This increased rate of degradation may be due to reactions with organic material, microorganisms, and other system additives and contaminants. Further, higher concentrations of glutaraldehyde may have inhibited microbial degradation, resulting in the decreased decay rates seen at 100 mg L^{-1} and 500 mg L^{-1}.

Although the degradation experiments employing glutaraldehyde and Disinfekt 1000® utilized slightly different treatment conditions (i.e., the level of filtration of the HRW and the water-sediment ratio), the half-life estimates for glutaraldehyde are comparable. These values are particularly close for the natural water-only and natural water-sediment treatments. This indicates that the surfactant adjuvant did not appreciably impede glutaraldehyde degradation, and the decay rate of both biocides is similar.

Results from NaOCl experiments indicate that hypochlorite degrades rapidly under most exposure conditions. Degradation was more rapid in filtered HRW than filtered WW, most likely due to the presence of dissolved or-

ganic matter (DOM). This suggests that even in water free of sediments or particulate matter, NaOCl may rapidly lose biocidal strength if there is a large amount of DOM. The results from the other set of degradation experiments indicate that chlorine concentrations will only remain relatively constant if the water is free of interfering material. The only two test conditions meeting these criteria were for exposures in sterile DW (deionized city water) and at 500 mg L^{-1} in unfiltered HRW. For these test conditions, NaOCl remained relatively constant over a 96 h period. In contrast, NaOCl concentrations decreased substantially unfiltered HRW at concentrations of 10 and 100 mg L^{-1}. This decay was augmented by the presence of sediments. In both the 10 and 100 mg L^{-1} NaOCl concentrations in sediment and unfiltered HRW, total chlorine concentrations decreased to less than 1 mg L^{-1} within 2 h after the solutions were made. The total chlorine for exposures, even as high as 500 mg L^{-1} NaOCl, reached nearly 0 mg L^{-1} over 96 h in the presence of sediment. These results indicate that high concentrations of hypochlorite will likely be needed to treat transoceanic NOBOB vessels, especially if they are carrying sediments or water with a high organic load. The presence of organic material will substantially decrease NaOCl efficacy with respect to ballast water treatment; however, the rapid degradation rate provides a potential advantage with respect to environmental impacts, since most of the biocidal potential will be gone upon release into receiving waters.

5. REFERENCES

ASTM. Standard Test Method for Biodegradation by a Shake-Flask Die-Away Method. E1279-89. Annual Book of ASTM Standards, Volume 11.05 Biological Effects and Environmental Fate; Biotechnology; Pesticides. Section 11 Water and Environmental Technology, American Society for Testing and Materials, West Conshohocken, PA (1998).

Bailey, S.A., I.C. Duggan, C.D.A. van Overdijk, P.T., Jenkins, and H.J. MacIsaac. Viability of invertebrate diapausing eggs collected from residual ballast sediment. *Limnology and Oceangraphy* (2003 In press).

Dermott, R., J. Witt, Y.M. Um, and M. González. Distribution of the Ponto-Caspian amphipod *Echinogammarus ischnus* in the Great Lakes and replacement of native Gammarus fasciatus. *Journal of Great Lakes Research* 24: 442-452 (1998).

Farley, R.B. Analysis of Overseas Vessel Transits into the Great Lakes and Resultant Distribution of Ballast Water, University of Michigan, Department of Naval Architecture and Marine Engineering, Report No. 331, October (1996).

Grigorovich, I.A. and H.J. MacIsaac. First record of *Corophium mucronatum Sars* (Crustacea : Amphipoda) in the Great Lakes. *Journal of Great Lakes Research* 25: 401-405 (1999).

Klerks, P.L., P.C. Fraleigh, and J.E. Lawniczak . Effects of the exotic zebra mussel (*Dreissena polymorpha*) on metal cycling in Lake Erie. *Canadian Journal of Fisheries and Aquatic Sciences* 54:1630-1638 (1997).

Leung, H.-W. Aerobic and anaerobic metabolism of glutaraldehyde in a river-water system. *Archives of Environmental Contamination and Toxicology* 41:267-273 (2001a).

Leung, H.-W. 2001b. Ecotoxicology of glutaraldehyde: Review of environmental fate and effects studies. *Ecotoxicology and Environmental Safety* 49:26-39 (2001b).

MacIsaac, H.J., I.A. Grigorovich, J.A. Hoyle, N.D. Yan, and V.E. Panov. Invasion of Lake Ontario by the Ponto-Caspian predatory cladoceran *Cercopagis pengoi*. *Canadian Journal of Fisheries and Aquatic Sciences* 56:1-5 (1999).

MacIsaac, H.J., T.C. Robbins, and M.A. Lewis. Modeling ships' ballast water as invasion threats to the Great Lakes. *Canadian Journal of Fisheries and Aquatic Sciences* 59:1245-1256 (2002).

Nalepa T.F., D.J. Hartson, J. Buchanan, J.F. Cavaletto, G.A. Lang, and S.J. Lozano. Spatial variation in density, mean size and physiological condition of the holarctic amphipod *Diporeia spp*. in Lake Michigan. *Freshwater Biology* 43:107-119 (2000).

Nicholls, K.H., G.J. Hopkins, and S.J. Standke. Reduced chlorophyll to phosphorus ratios in nearshore Great Lakes waters coincide with the establishment of dreissenid mussels. *Canadian Journal of Fisheries and Aquatic Sciences* 56:153-161 (1999).

NRC (National Research Council). Stemming the Tide: Controlling Introductions of Nonindigenous Species by Ships' Ballast Water. Committee on Ships' Ballast Operations and Marine Board Commission on Engineering and Technical Systems for the National Research Council. National Academy Press: Washington, DC (1996).

Pakulski, J.D., and Benner, R. An improved method for the hydrolysis and MBTH analysis of dissolved and particulate carbohydrates in seawater. *Mar. Chem*. 40:143-160 (1992).

Porter, K.G. and Y.S. Feig. The use of DAPI for identifying and counting aquatic microflora. *Limnology and Oceanography* 25(5):943-948 (1980).

Sawicki, E., Hauser, T.R., Stanley, T.W., and Elbert, W. The 3-methyl-2-benzothaizolone hydrazone test: Sensitive new methods for the detection, rapid estimation, and determination of aliphatic aldehydes. *Anal. Chem*. 33: 93-96 (1962).

Schloesser, D.W., W.P. Kovalak, G.D. Longton, K.L. Ohnesorg, and R.D. Smithee. Impact of zebra and quagga mussels (*Dreissena spp*.) on freshwater unionids (Bivalvia : Unionidae) in the Detroit River of the Great Lakes. *Amer. Midland Natural*. 140: 299-313 (1998).

Figures

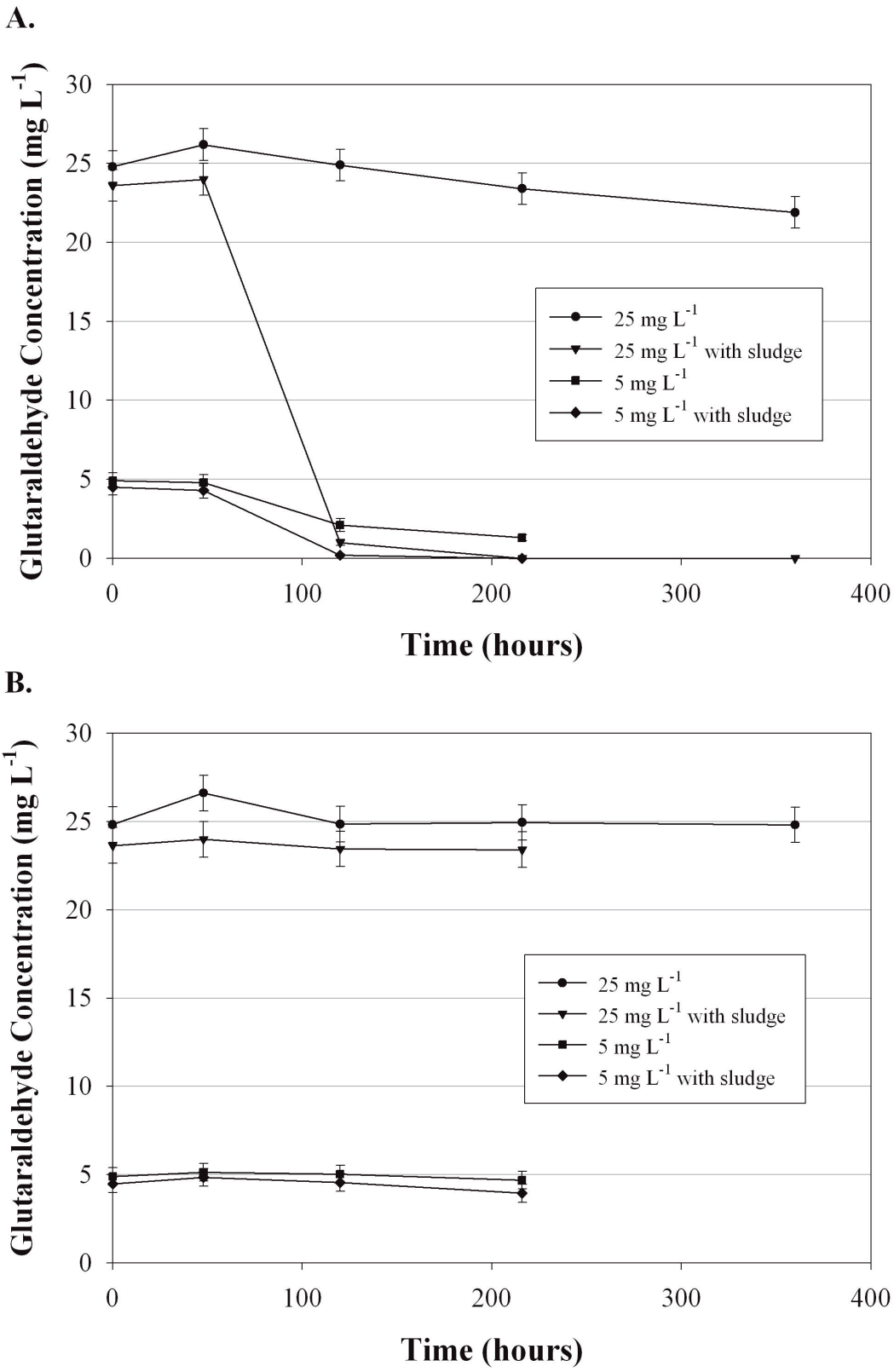

Figure 1. Degradation rate of glutaraldehyde with and without addition of sludge mixture. Data are provided for 25°C (Fig. A) and for 4°C (Fig. B).

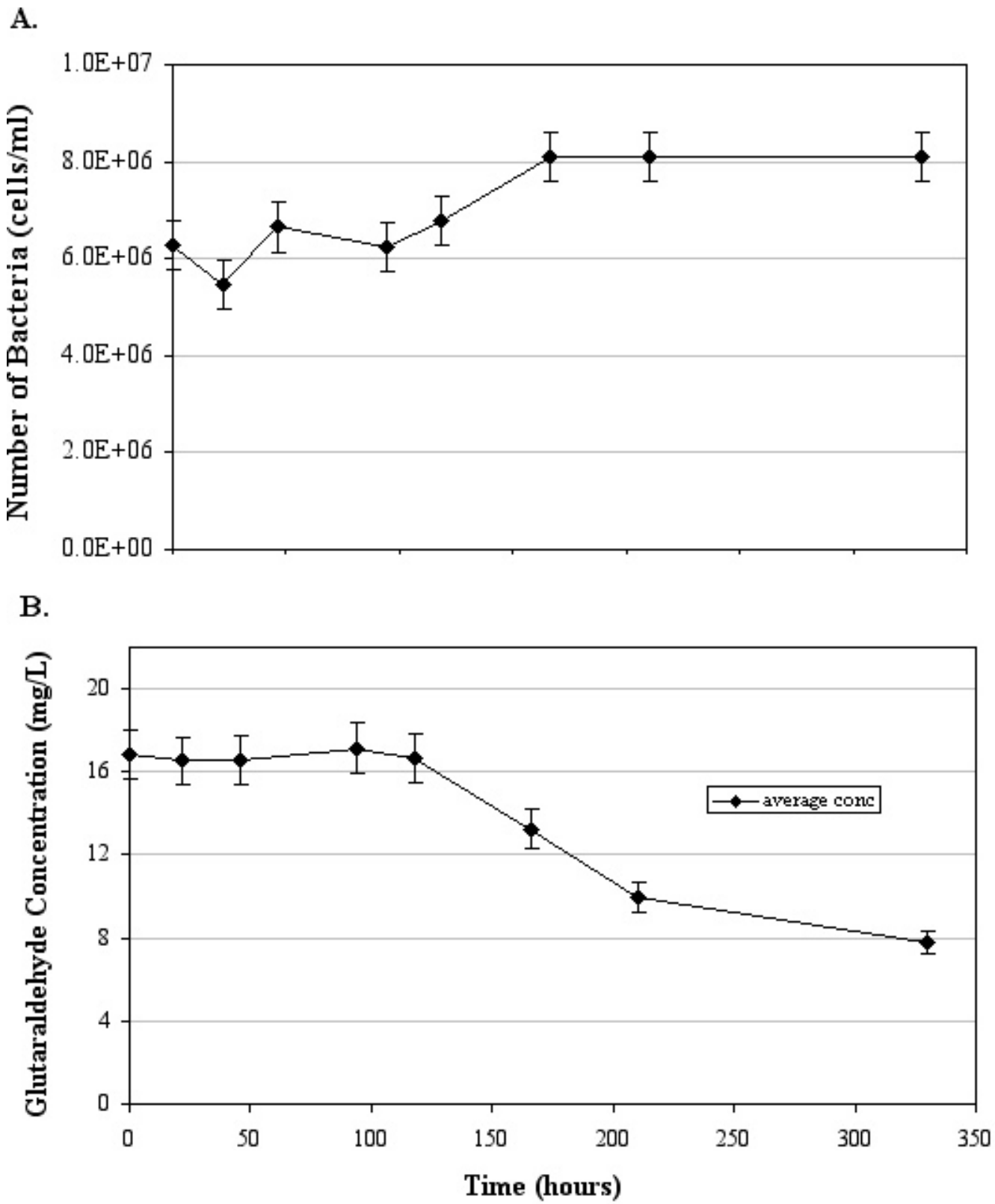

Figure 2. Bacterial counts (A) and degradation (B) of glutaraldehyde at 25°C.

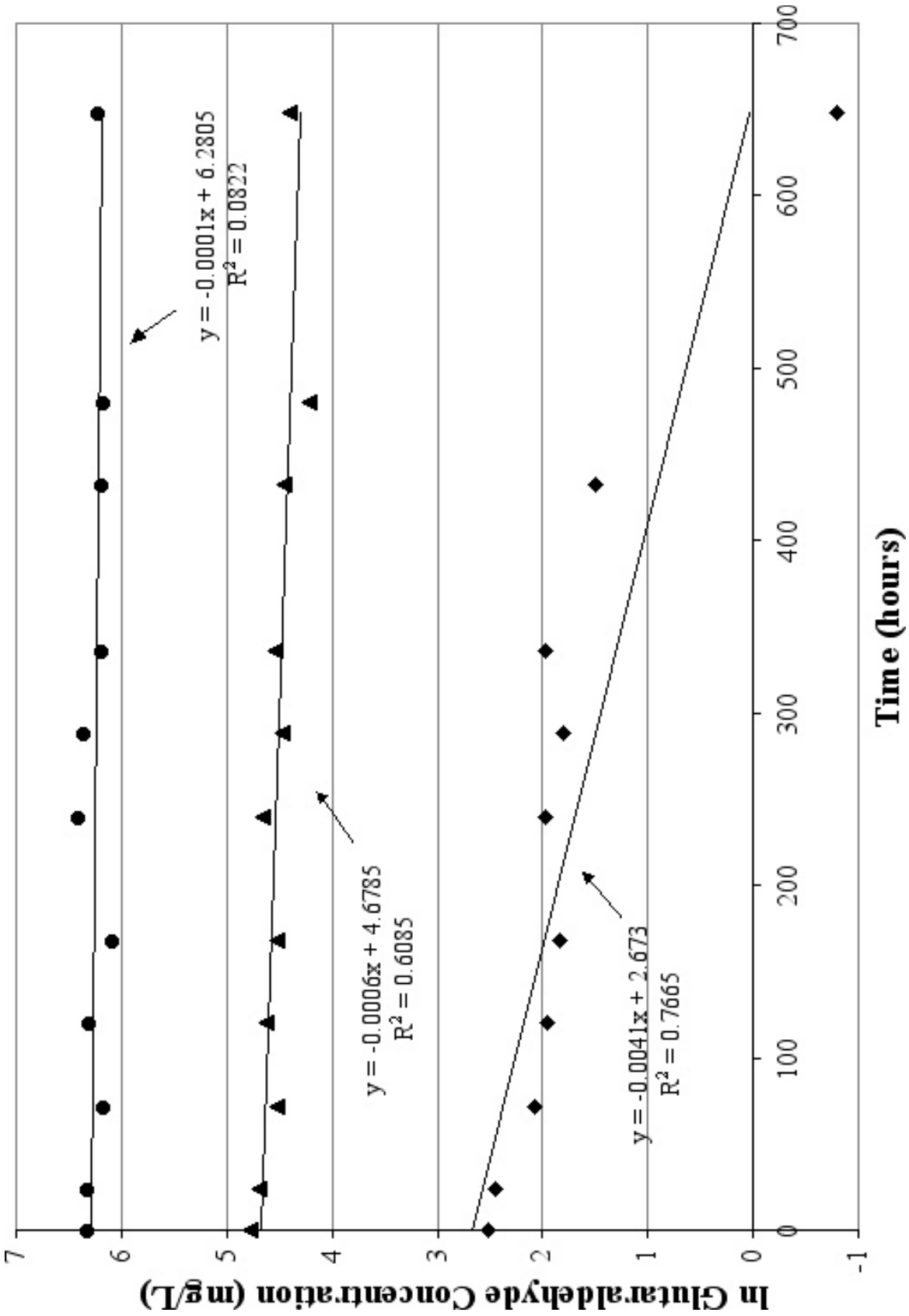

Figure 3. Degradation of glutaraldehyde under natural water-sediment conditions at 5°C. ▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

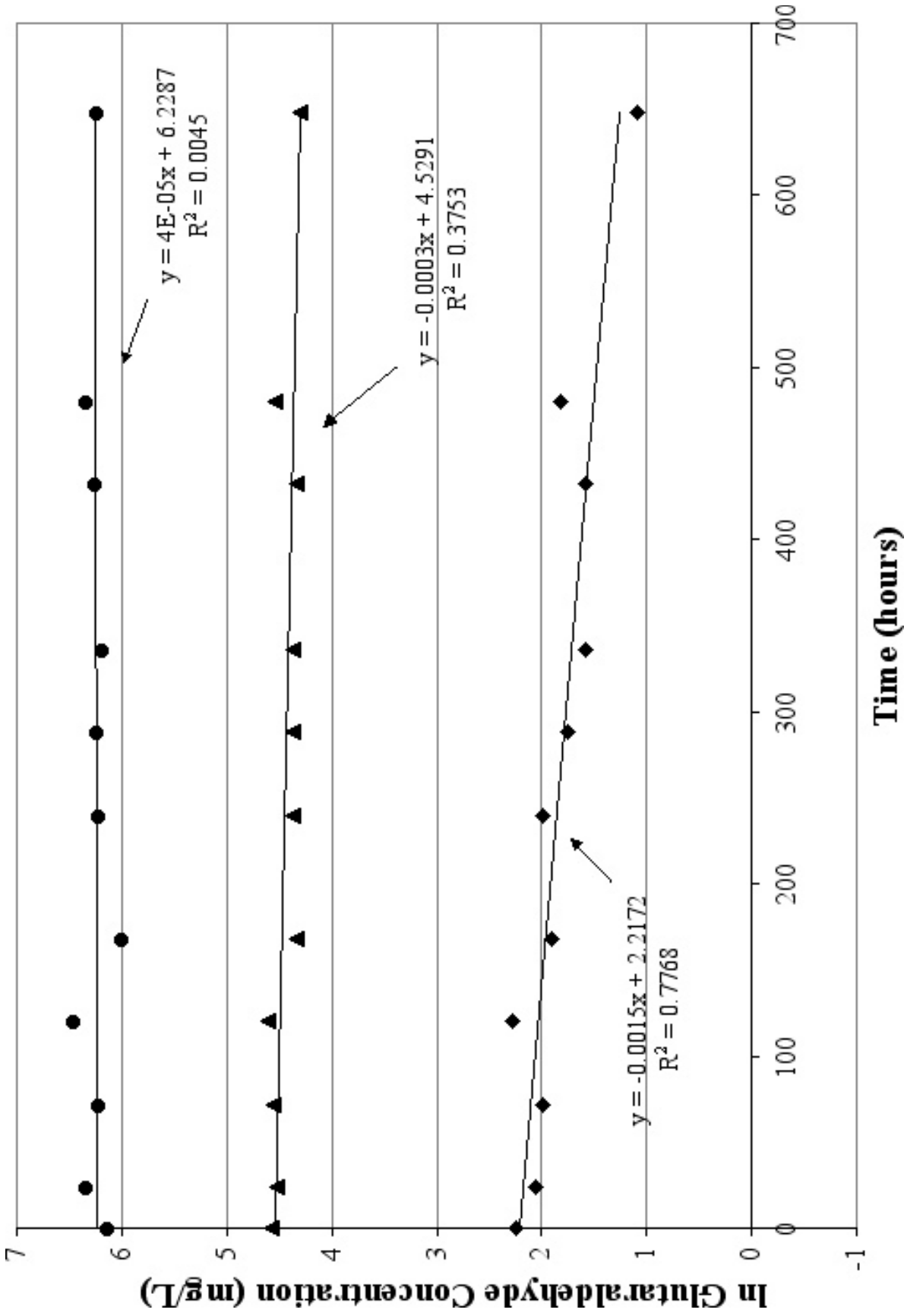

Figure 4. Degradation of glutaraldehyde under sterile water-sediment conditions at 5°C.
▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

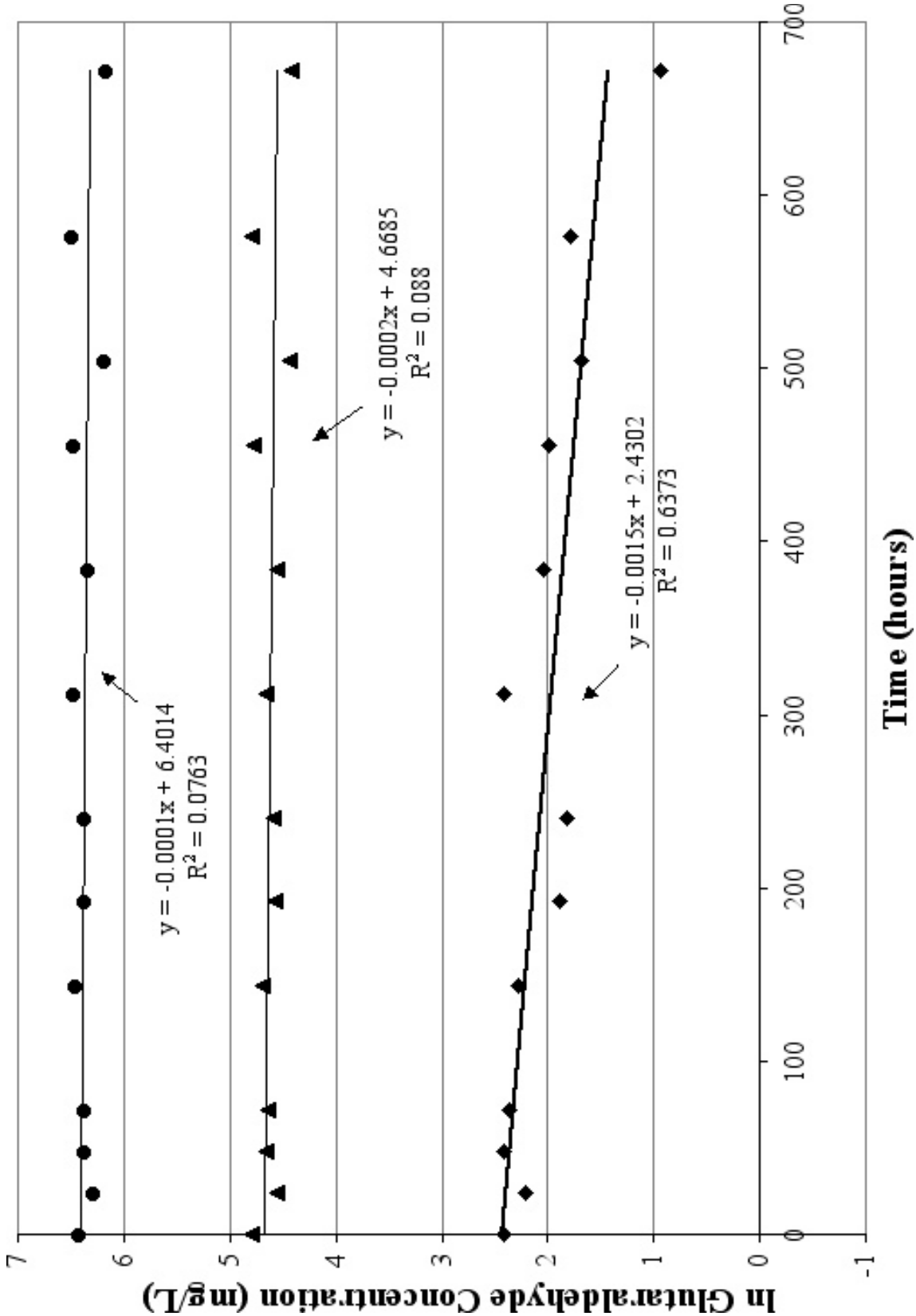

Figure 5. Degradation of glutaraldehyde under natural water-only conditions at 15°C.
▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

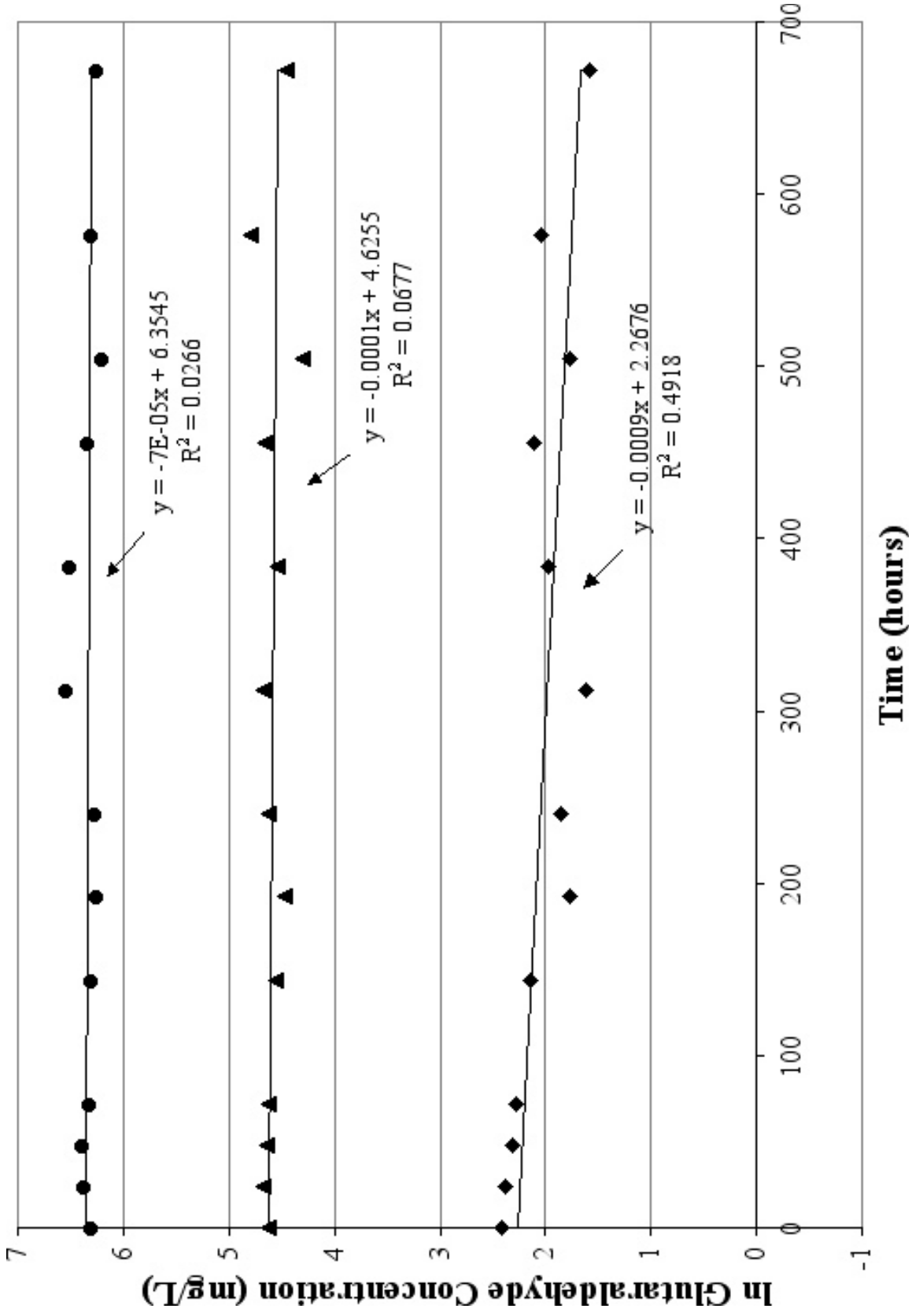

Figure 6. Degradation of glutaraldehyde under sterile water-only conditions at 15°C.
▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

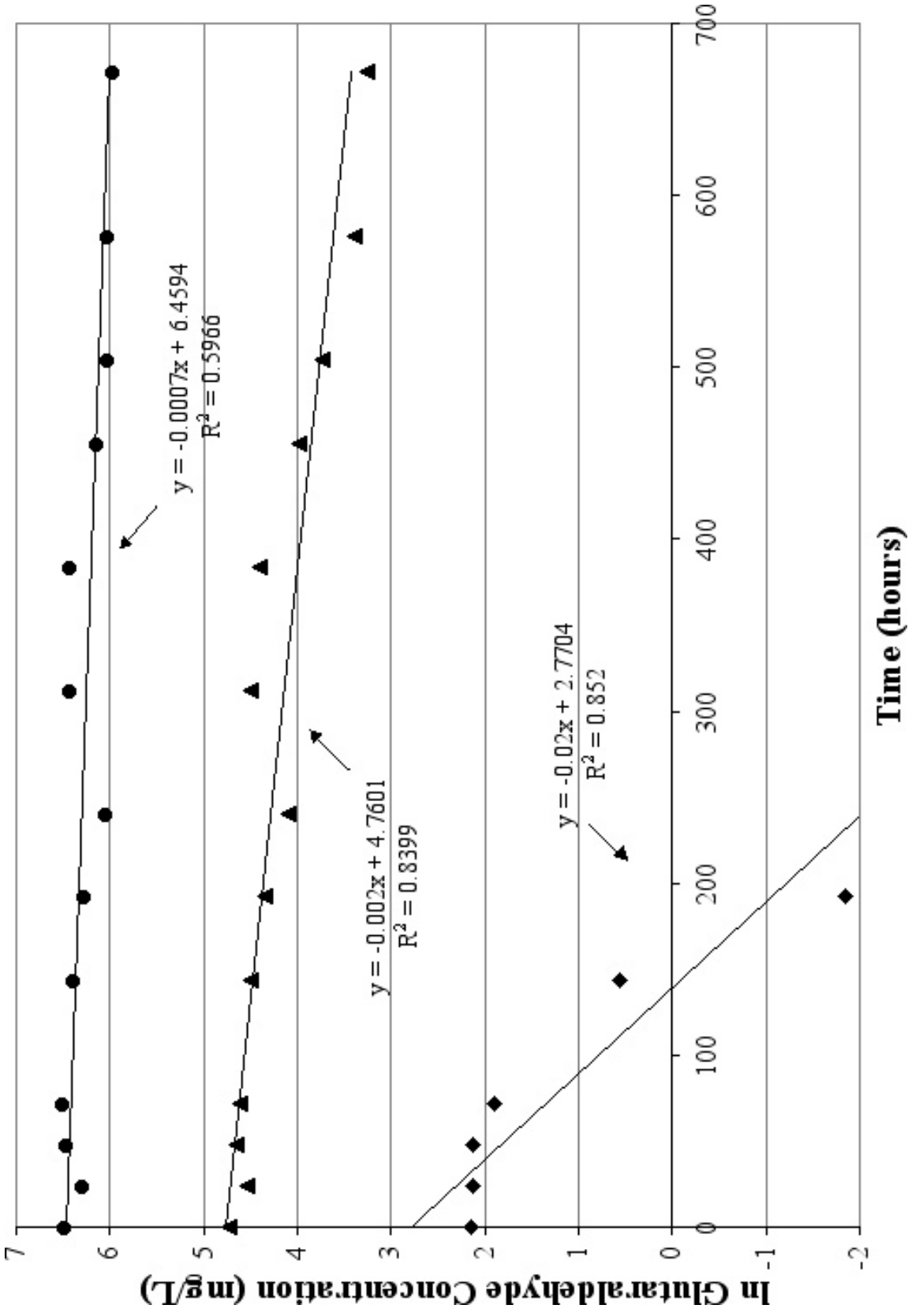

Figure 7. Degradation of glutaraldehyde under natural water-sediment conditions at 15°C. ▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

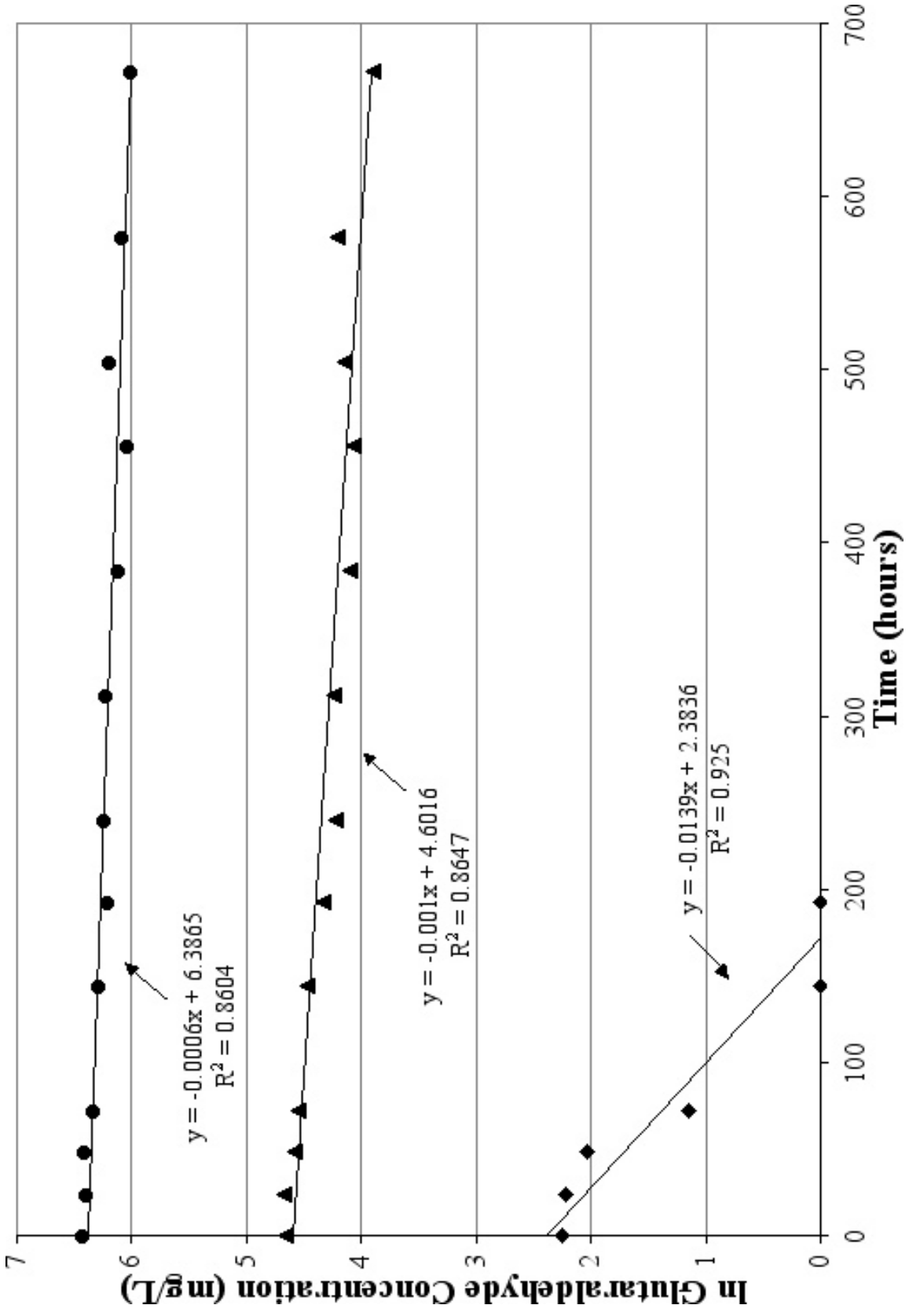

Figure 8. Degradation of glutaraldehyde under sterile water-sediment conditions at 15°C. ▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

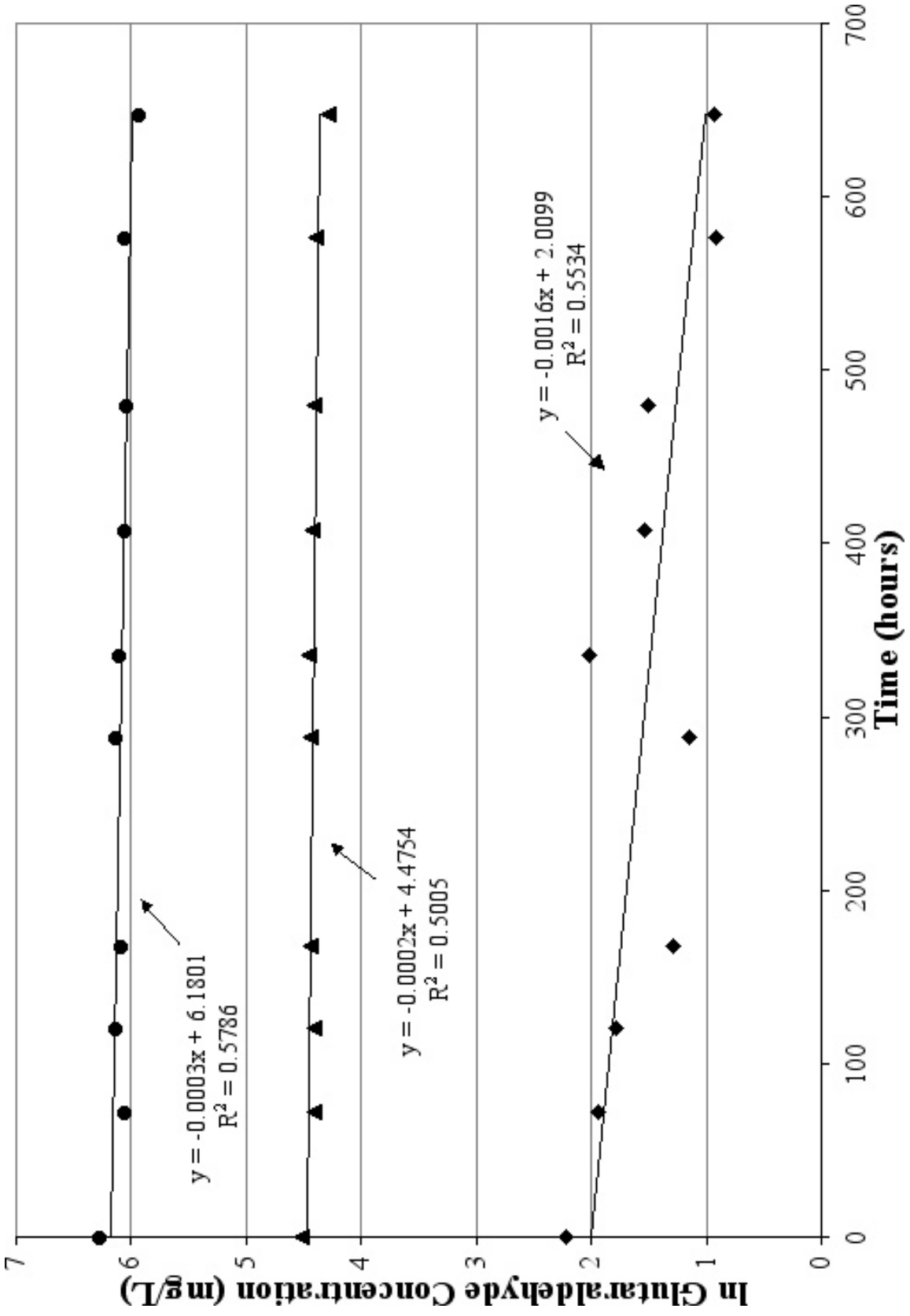

Figure 9. Degradation of glutaraldehyde under natural water-only conditions at 25°C.
▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

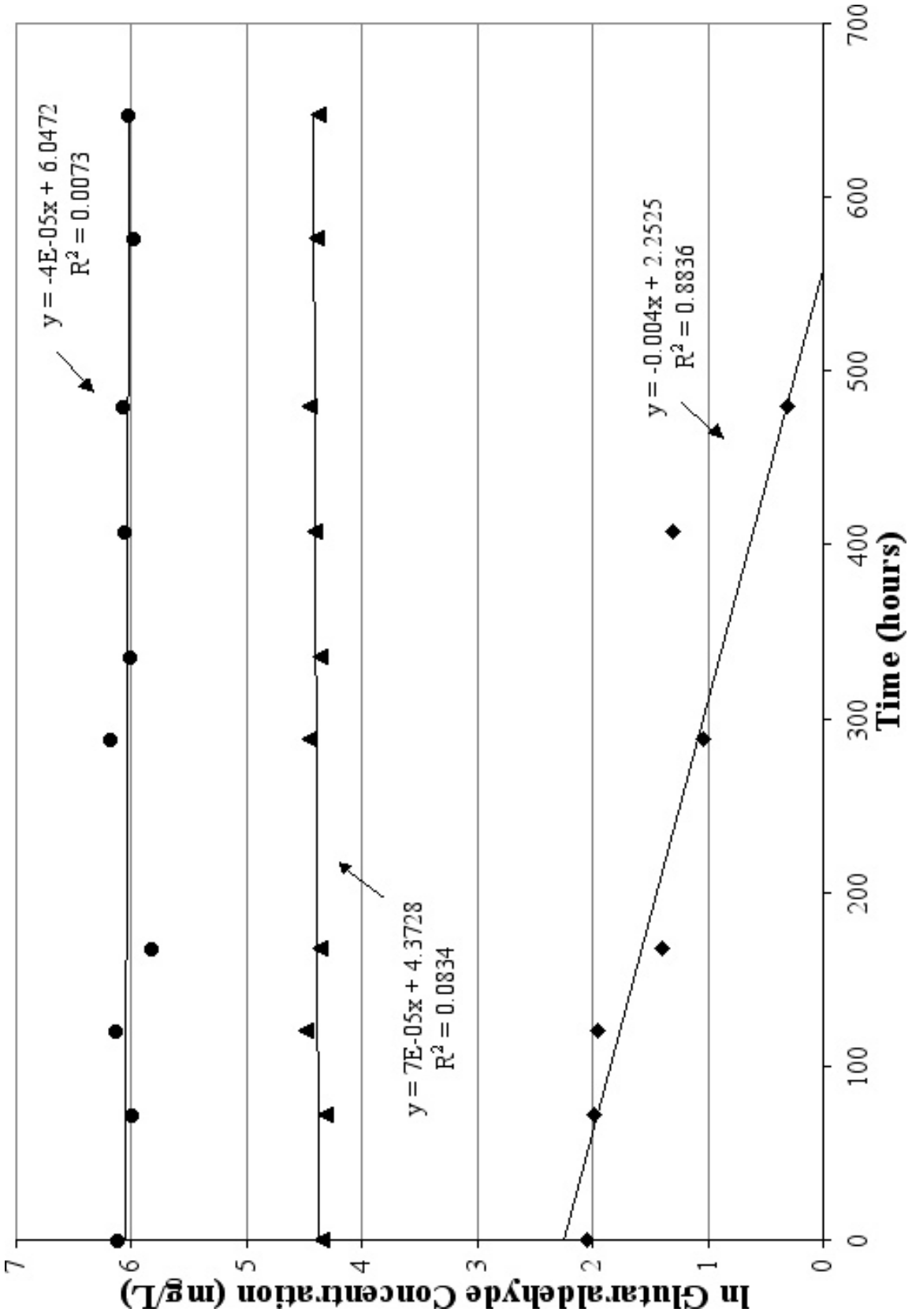

Figure 10. Degradation of glutaraldehyde under sterile water-only conditions at 25°C.
▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

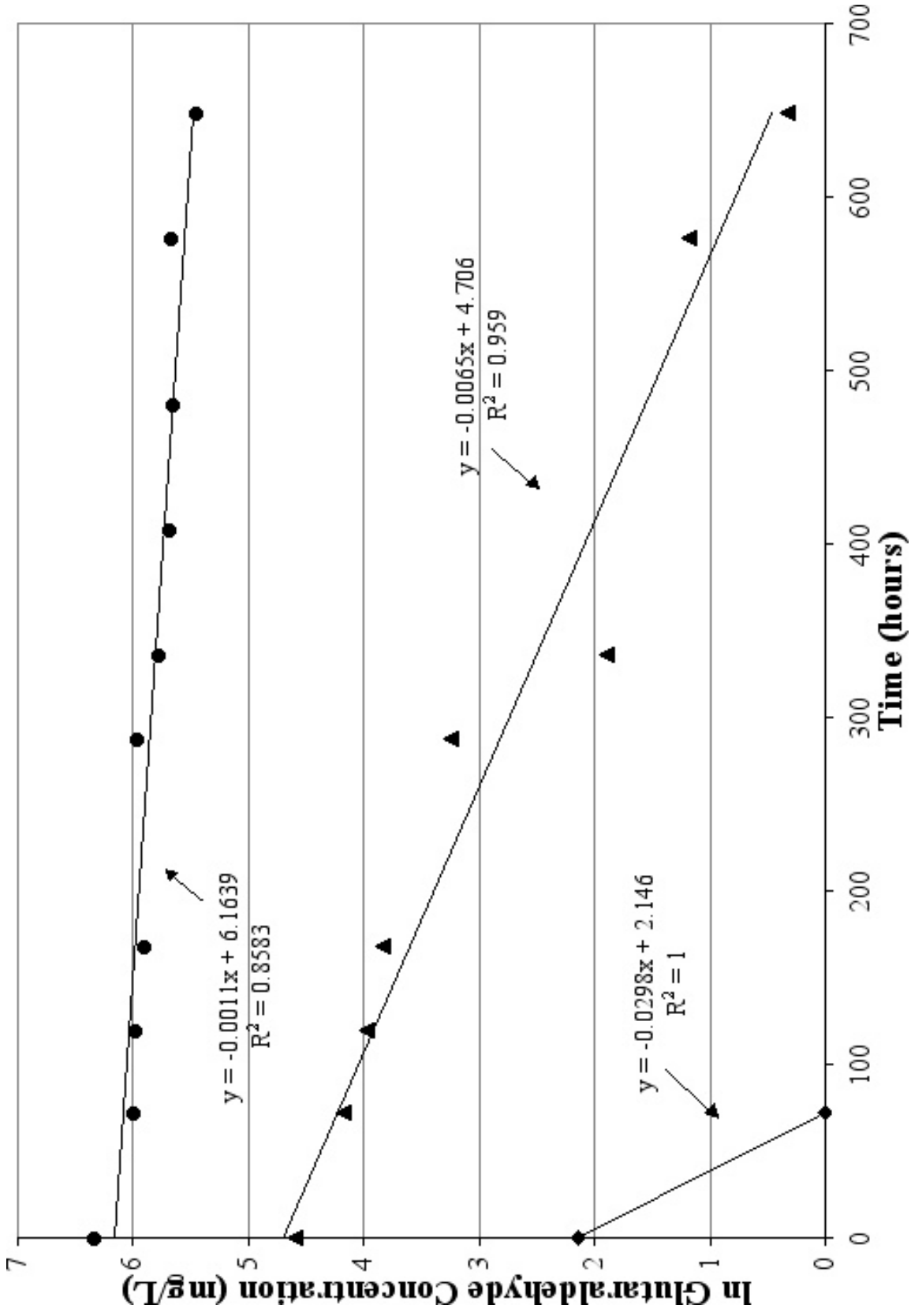

Figure 11. Degradation of glutaraldehyde under natural water-sediment conditions at 25°C. ▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

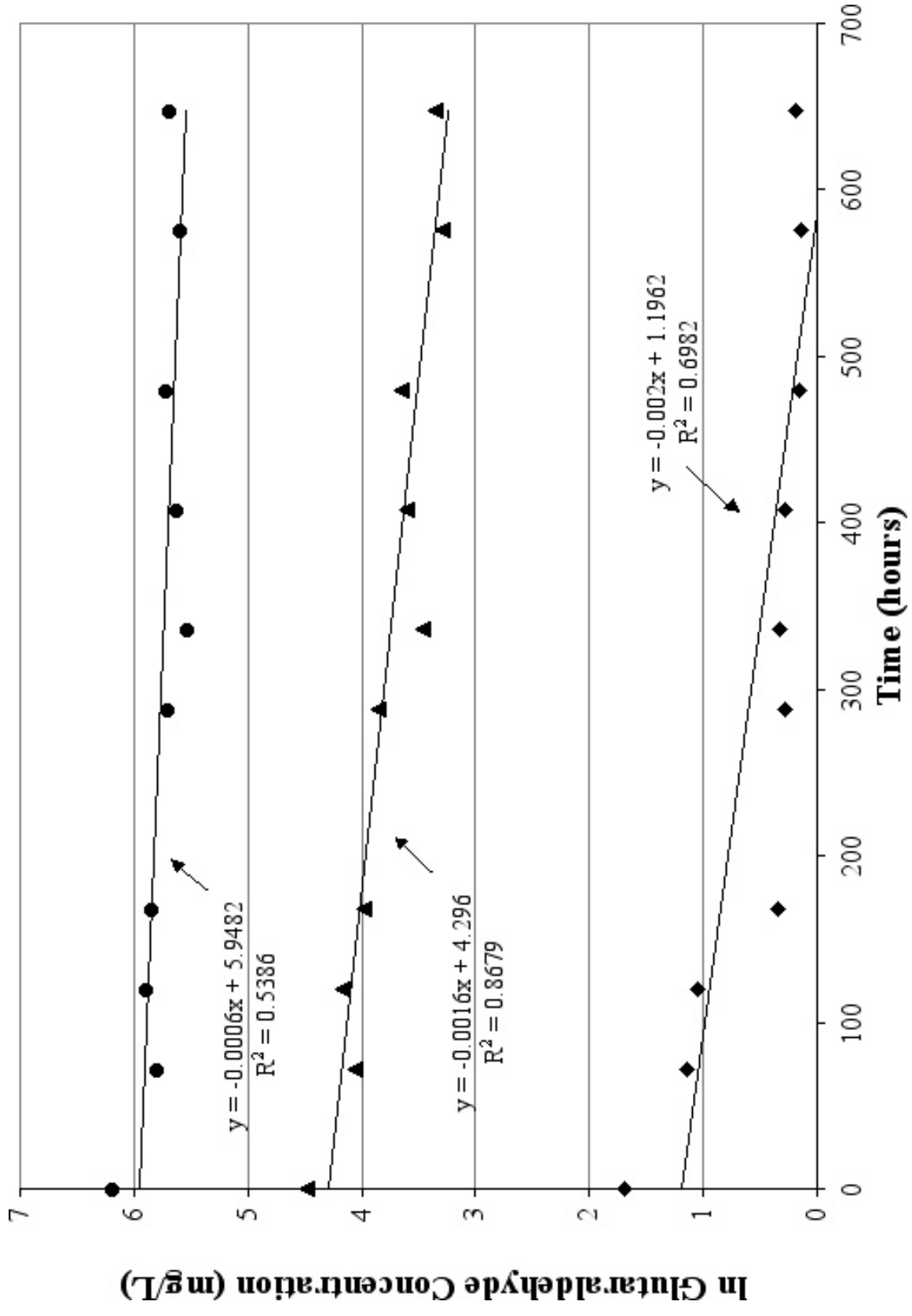

Figure 12. Degradation of glutaraldehyde under sterile water-sediment conditions at 25°C. ▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

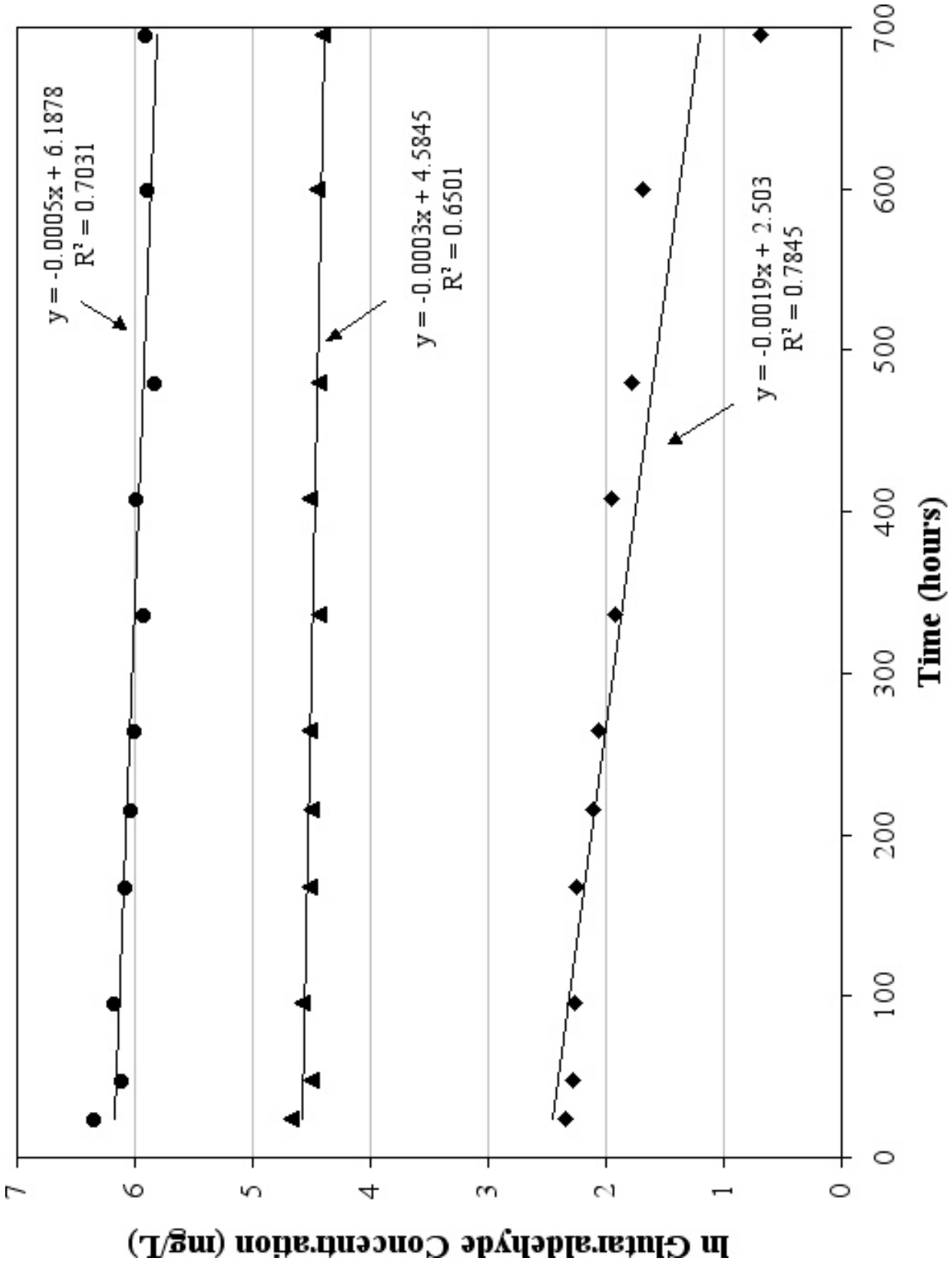

Figure 13. Degradation of glutaraldehyde in Disinfekt 1000, under natural water-only conditions at 25 °C. ▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

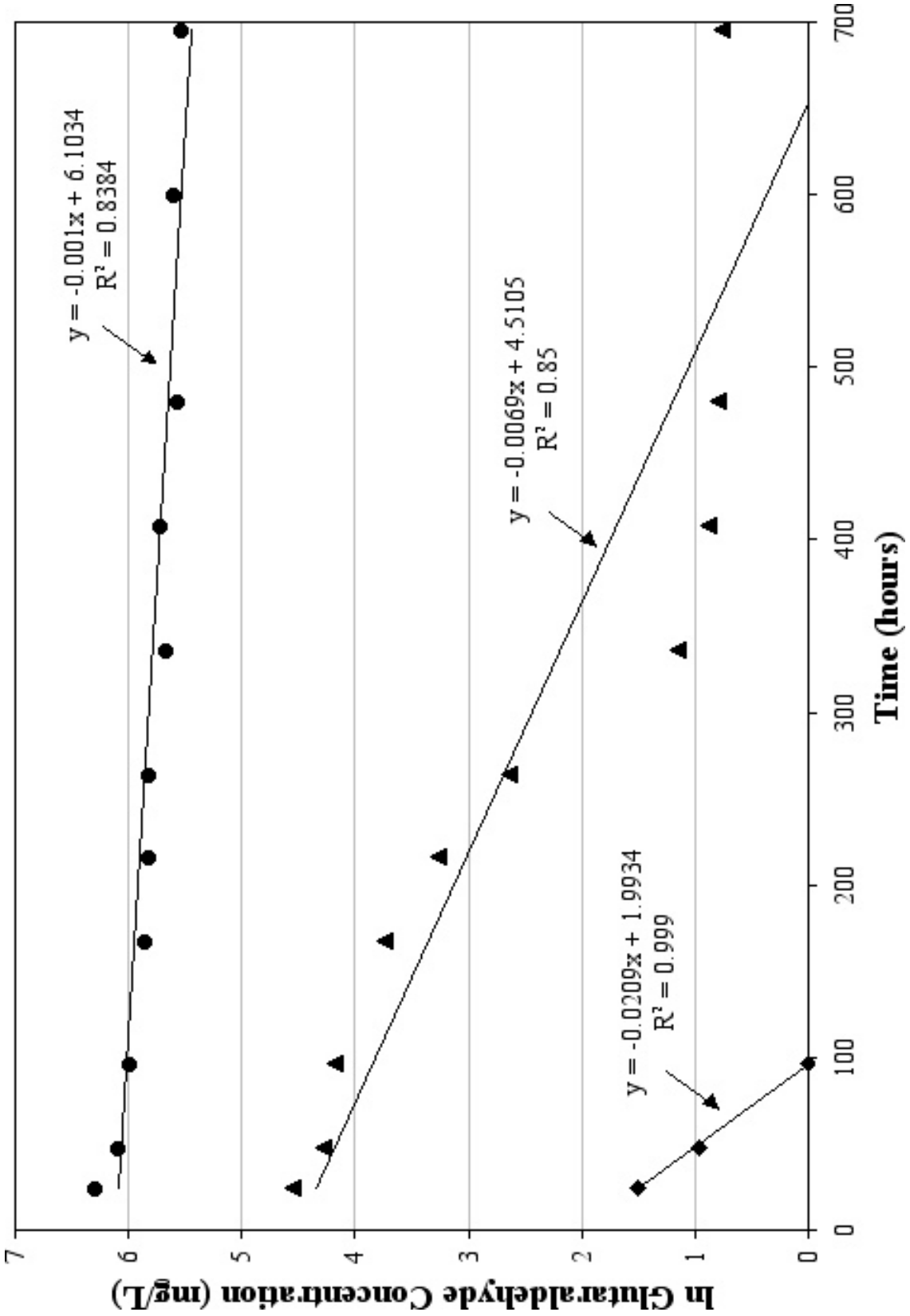

Figure 14. Degradation of glutaraldehyde in Disinfekt 1000, under natural water-sediment conditions at 25°C. ▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration (prefiltered Huron River water and Gallup Park sediment in a ratio of 4:1.)

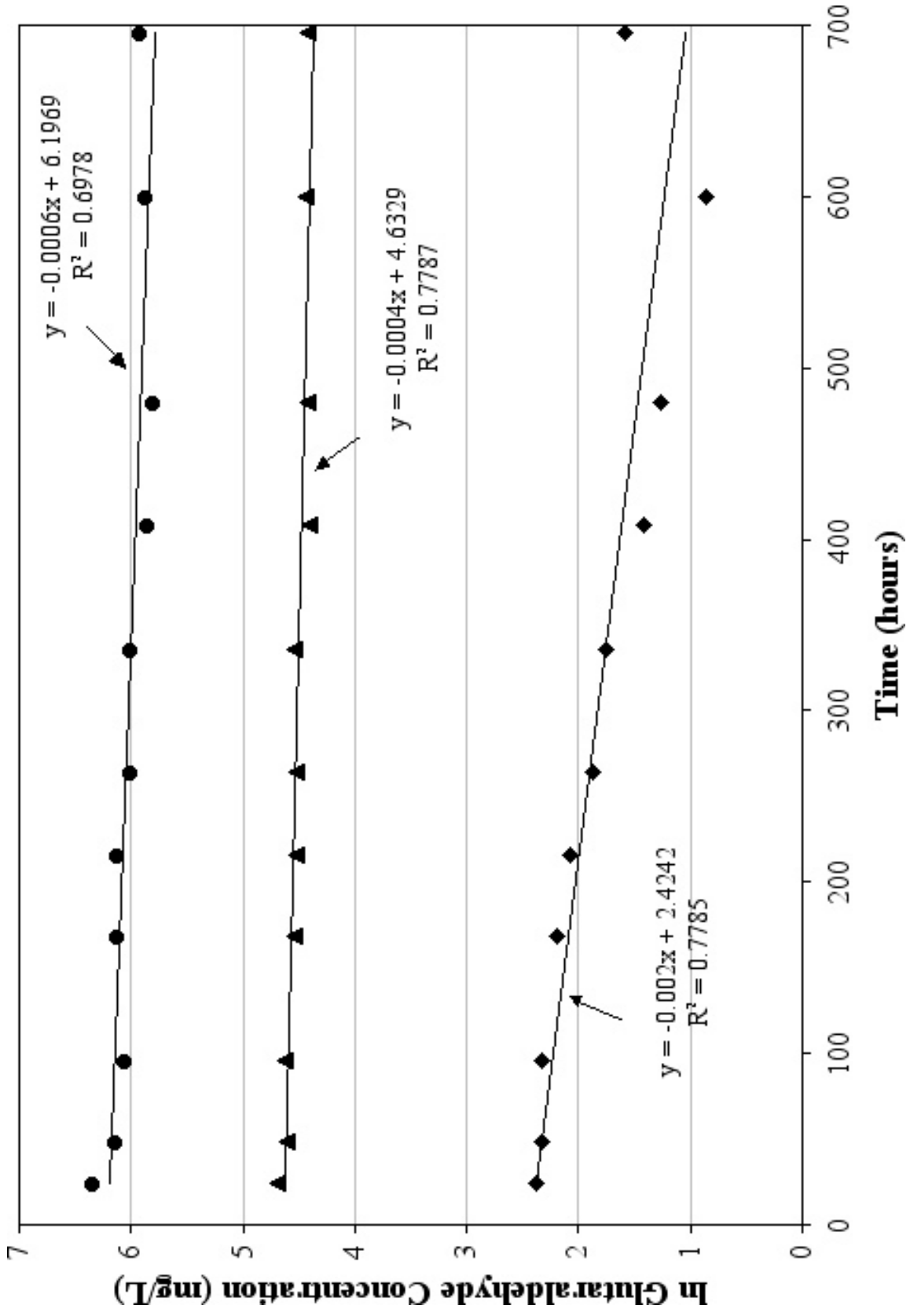

Figure 15. Degradation of glutaraldehyde in Disinfekt 1000, under sterile water-only conditions at 25°C. ▲ 500 mg L^{-1} initial concentration; ● 100 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration.

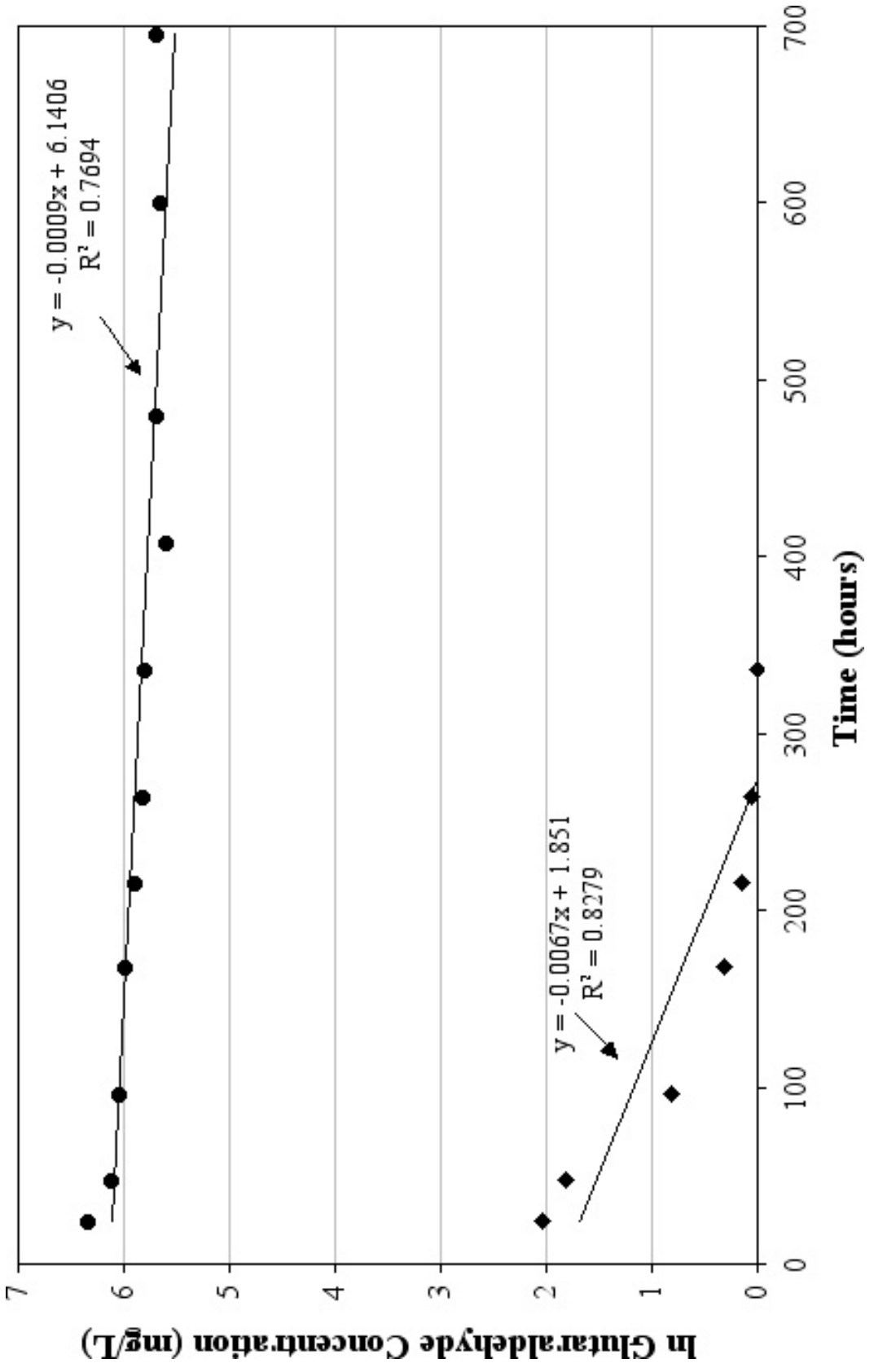

Figure 16. Degradation of glutaraldehyde in Disinfekt 1000, under sterile water-sediment conditions at 25°C. ▲ 500 mg L^{-1} initial concentration; ◆ 10 mg L^{-1} initial concentration. The 100 mg L^{-1} concentration was accidentally destroyed.

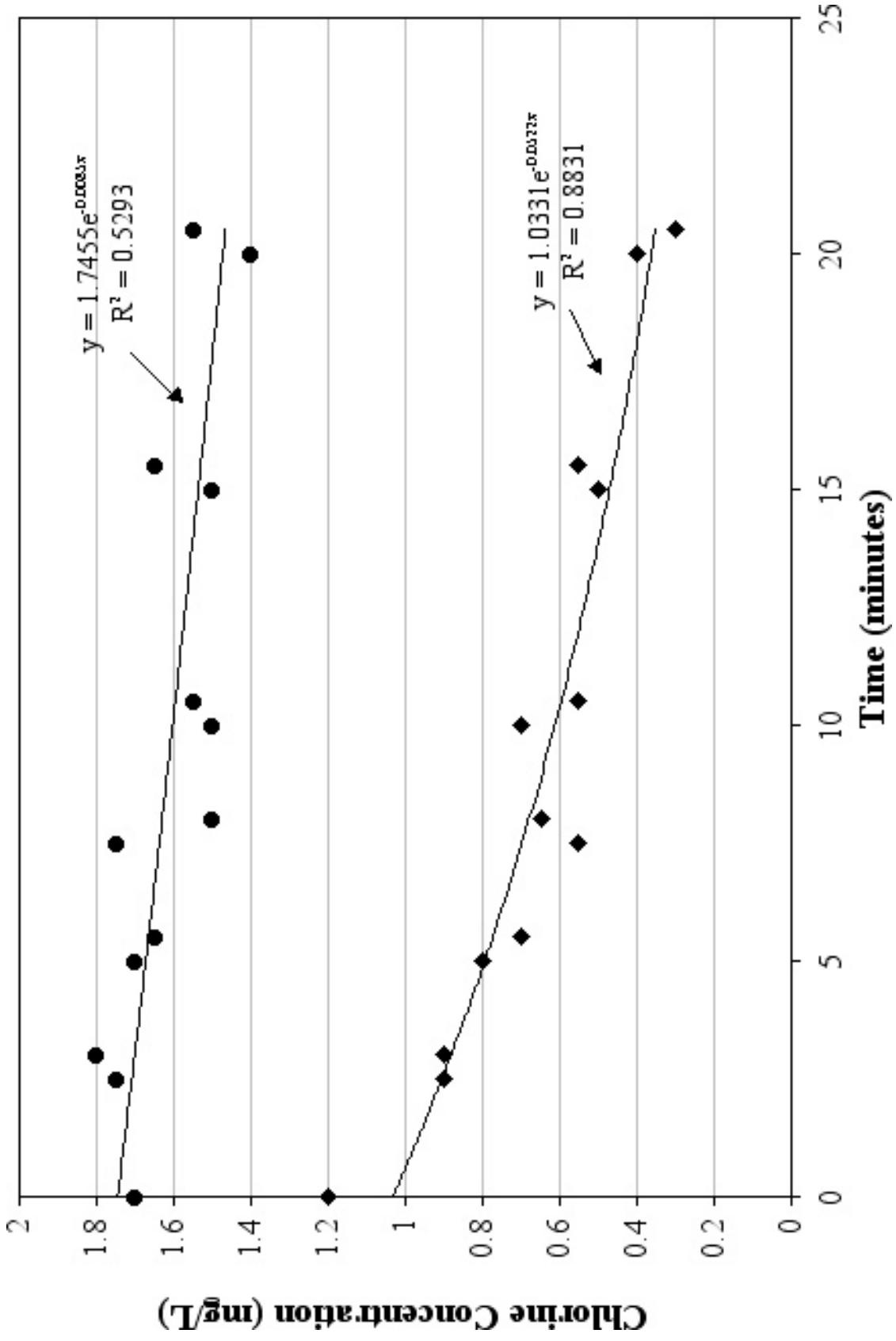

Figure 17. Degradation data for NaOCl over a 20.5 min period. Solutions were made in filtered Huron River water (HRW) and filtered well water (WW). Fit with exponential equation. ▲ 2 mg L^{-1} initial concentration; ◆ 1 mg L^{-1} initial concentration.

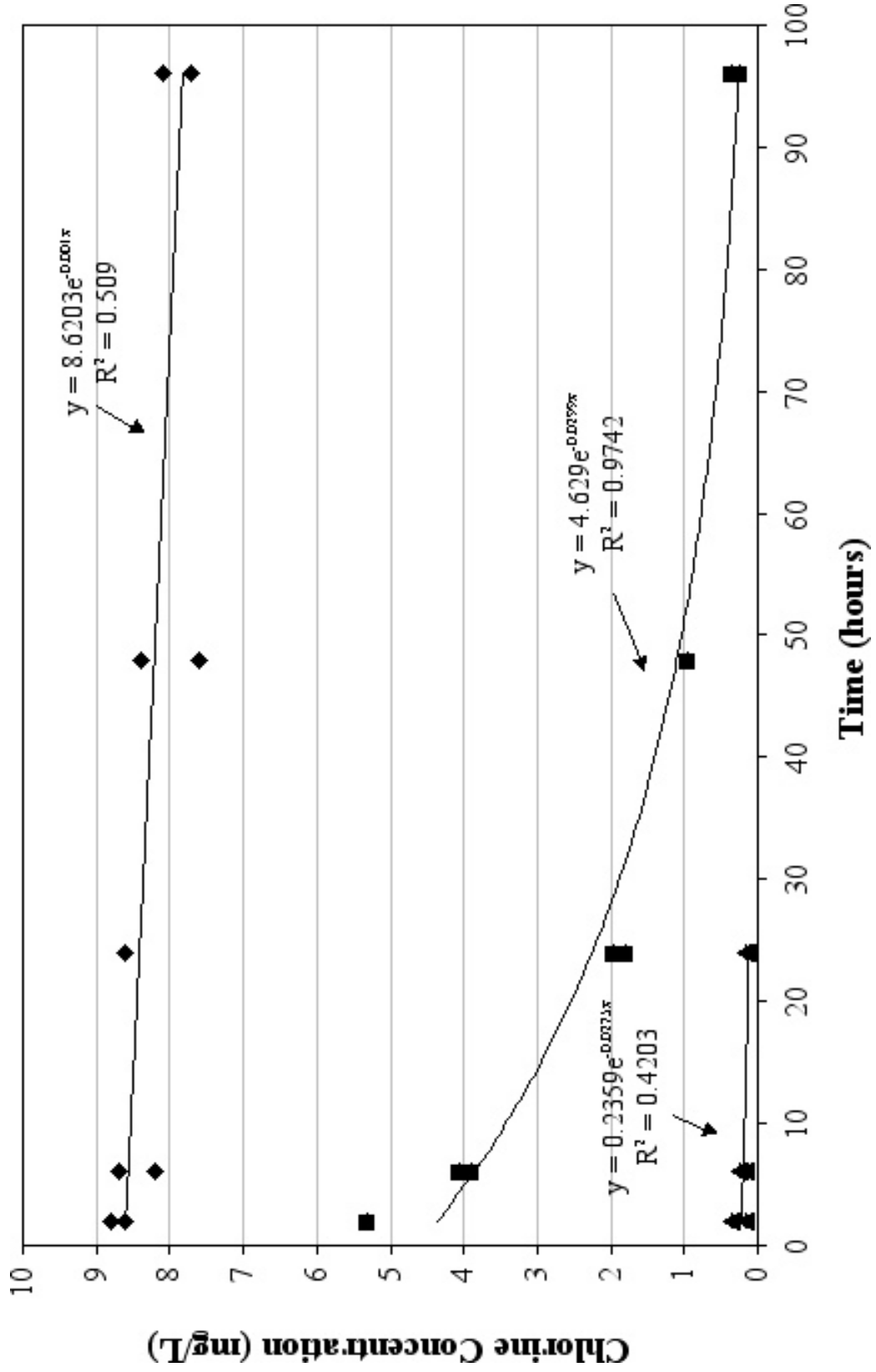

Figure 18. Ninety-six hour degradation of sodium hypochlorite starting with a 10 mg L^{-1} nominal hypochlorite concentration. ◆ deionized city water (DW); unfiltered Huron River water (HRW); ● unfiltered Huron River water plus sediments (from Gallup Park, 8:1 water-sediment ratio).

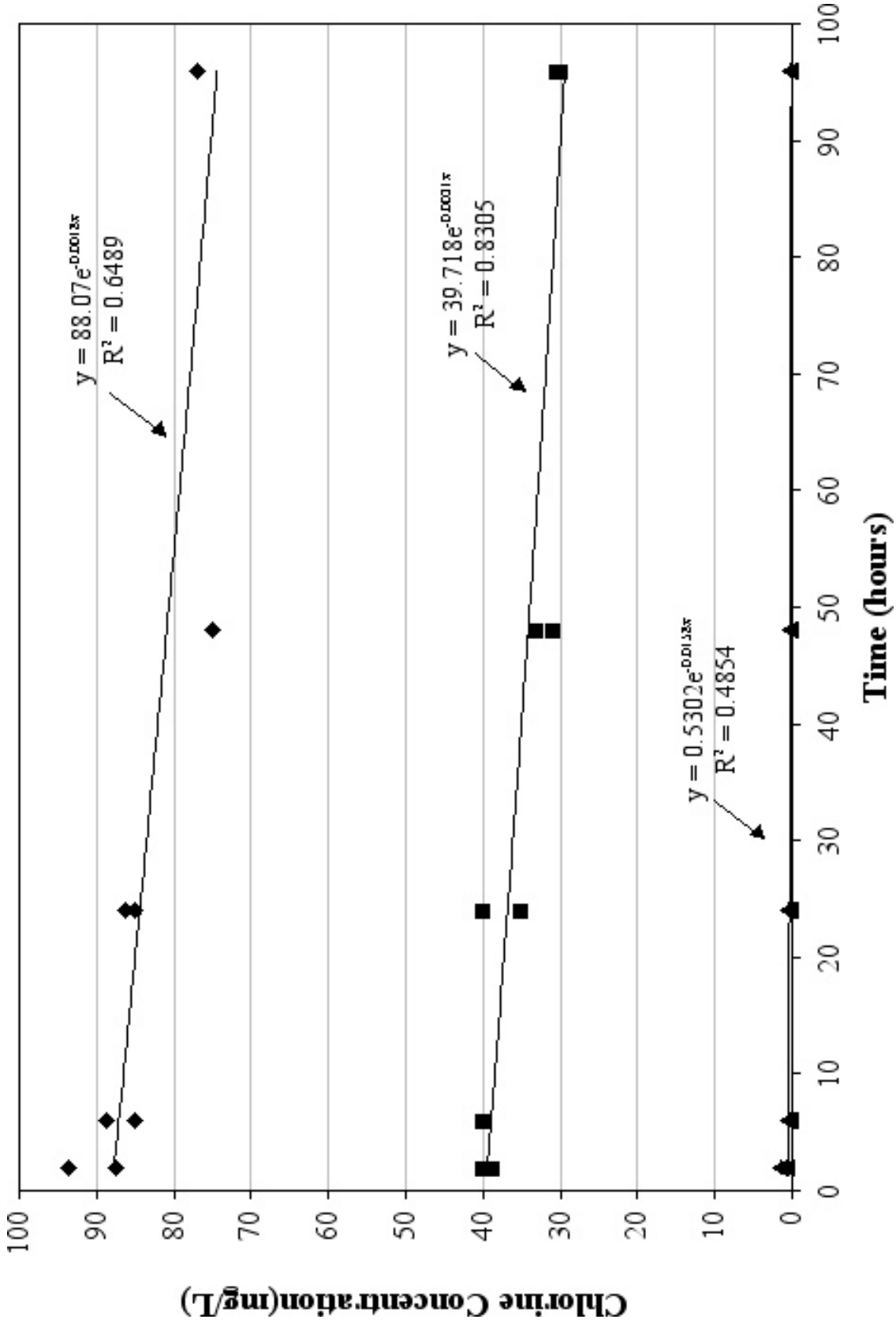

Figure 19. Ninety-six hour degradation of sodium hypochlorite starting with a 100 mg L^{-1} nominal hypochlorite concentration. ◆ deionized city water (DW); unfiltered Huron River water (HRW); ● unfiltered Huron River water plus sediments (from Gallup Park, 8:1 water-sediment ratio).

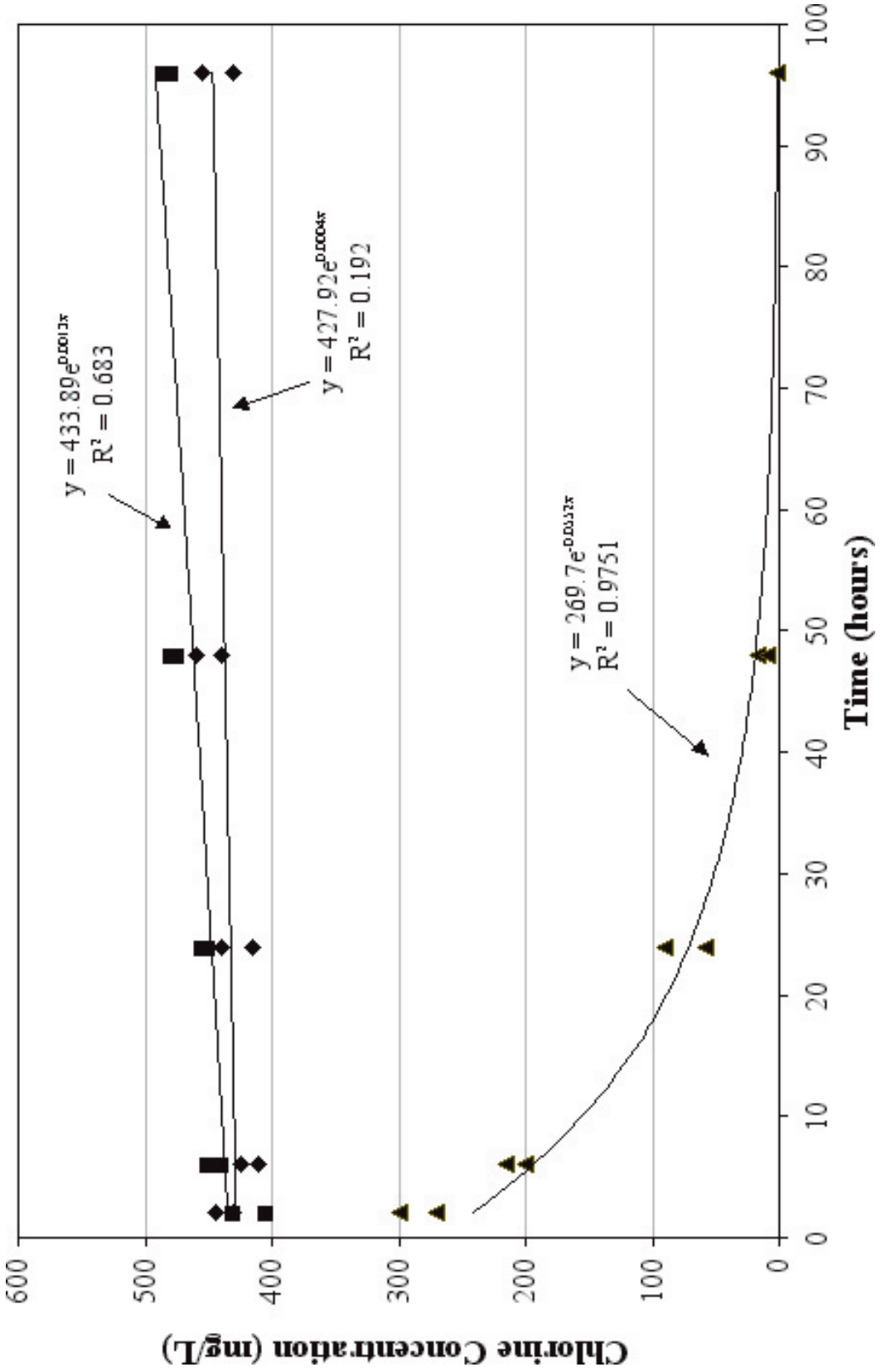

Figure 20. Ninety-six hour degradation of sodium hypochlorite using a nominal initial hypochlorite concentration of 500 mg L^{-1}. ◆ deionized city water (DW); unfiltered Huron River water (HRW); ● unfiltered Huron River water plus sediments (from Gallup Park, 8:1 water-sediment ratio).