United States
Environmental Protection
Agency

Water Engineering
Research Laboratory
Cincinnati OH 45268

Research and Development

EPA/600/S2-86/045 June 1986

EPA

Project Summary

Toxic Substance Removal in Activated Sludge and PAC Treatment Systems

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The addition of powdered activated carbon (PAC) to activated sludge treatment systems to enhance removal of specific toxic organic compounds from wastewater was evaluated. Little prior information existed on the behavior of toxic organics during activated sludge treatment. Thus a considerable effort was directed toward identifying and quantifying the fate of specific compounds in conventional activated sludge systems as well as in those to which carbon was added. Nine organic compounds encompassing a range of solubility, volatility, biodegradability, and adsorptive properties were studied along with selected commercial PAC's recommended for use in integrated activated sludge/carbon treatment systems. Completely-mixed-flow bioreactors equipped with internal clarifiers and air-tight lids were used to study the removal of each compound. Completely mixed batch rate and equilibrium studies were conducted to quantify the removal mechanisms of volatilization, biodegradation, biosorption, and carbon adsorption.

Results from steady-state bioreactor studies showed that the addition of less than 100 mg/L PAC to the influent did not enhance the removal of the biodegradable compounds benzene, toluene, ethylbenzene, o-xylene, chlorobenzene, and nitrobenzene. Significantly improved removals of the poorly degradable and nonbiodegradable compounds 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and lindane occurred at influent powdered carbon concentrations in the 12.5- to 25-mg/L range. Influent powdered carbon concentrations of 100 mg/L effected overall removals of greater than 90%. The addition of PAC not only reduced effluent concentrations but also reduced the amounts of the volatile compounds stripped to the atmosphere.

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 presence of toxic organic compounds in receiving waters and water supplies has modified the emphasis of wastewater treatment during the past several decades. Wastewater treatment systems historically have been designed to remove BOD, suspended solids, pathogenic organisms, and nitrogen and phosphorus, but the removal of these substances alone is no longer sufficient to protect the quality of receiving waters. Current discharge regulations impose limitations on specific toxic substances such as the 114 organic compounds designated as priority pollutants by the U.S. Enviromental Protection Agency (EPA).

The presence of toxic organic compounds in municipal and industrial wastewaters necessitates an understanding of the capabilities of conventional wastewater treatment systems for removing such substances. Some organic compounds are adequately removed, but the specific removal mechanisms must be identified and quantified so that treatment systems can be operated to achieve maximum effectiveness. Other compounds are not removed to levels considered acceptable for discharge. Treatment of these substances will require modifications or alternatives to existing treatment systems.

Various modifications and alternatives to conventional biological treatment processes have been suggested and evaluated in bench-, pilot-, and full-scale treatment systems during the past several decades. The addition of PAC to the aeration basins of activated sludge facilities (a process known as PACT*) has emerged as an attractive, integrated application of both biological degradation and adsorption technology to wastewater treatment for removal of organic compounds. Though this integrated process was originally introduced as a method for upgrading the performance of activated sludge systems with respect to conventional parameters, its potential ability to remove toxic and carcinogenic organic compounds may be at least as significant. However, little information exists on either the fate of specific organic compounds during such treatment or on the factors that control the effectiveness of their removal.

This project was designed to study the fate and behavior of specific organic compounds in bench-scale activated sludge and integrated activated sludge and carbon treatment systems. The effectiveness of adding PAC was evaluated by comparing the removals of specific compounds in integrated systems with removals in activated sludge systems.

Experimental Approach

Compounds Studied

Nine specific organic compounds were included in the study (Table 1). They encompass a broad range of volatility, biodegradability, and adsorptive properties. One feature of the study was the use of pollutants known to be present in municipal and industrial wastewaters and at concentrations representative of those actually measured in the field.

Adsorbents

Background adsorption studies were conducted with a variety of adsorbents to select one PAC as the primary adsorbent for use in the continuous-flow bioreactor studies. Based on adsorptive performance in equilibrium isotherm studies and commercial availability for wastewater treatment, Hydrodarco C (ICI Americas) was chosen as the primary adsorbent for the bioreactor studies.

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

Bioreactors

Completely-mixed-flow (CMF) bioreactors containing 10-L aeration sections and 1-L internal clarifiers were used to study the fate of the organic compounds during activated sludge and integrated activated sludge and carbon treatment. Each bioreactor was fitted with an air-tight lid that enabled collection and sampling of bioreactor off-gases for each organic compound. The air-tight lids, which were a unique feature of the experimental system, facilitated formulation of a mass balance for each compound and determination of its fate during treatment. A schematic diagram of the experimental system appears in Figure 1.

Removal Mechanisms

Batch equilibrium and rate studies were conducted to evaluate independently the mechanisms that affect the fate of organic compounds during activated sludge and integrated activated sludge and carbon treatment. Four removal mechanisms were identified: volatilization, biosorption, biodegradation, and PAC adsorption. A summary of each of these studies is given below. The full report details the experimental approach and complete results from each study.

Volatilization

Batch air-stripping studies were conducted over a range of aeration rates in 10-L bioreactors without activated sludge present to determine the rates at which individual compounds, were volatilized from the experimental system. First-order volatilization rate coefficients were determined from the slope of semi-logarithmic plots of concentration versus time. A linear relationship between the volatilization rate coefficient and the aeration rate was observed for each compound. Batch-generated volatilization rate coefficients were used to predict the fate of the seven volatile compounds in continuous-flow bioreactors without activated sludge. The agreement between the predicted and measured effluent and off-gas values (Table 2) demonstrates that volatilization was well characterized in the experimental system. The results indicated that volatilization effected at least 90% reduction of the volatile compounds in the aqueous concentrations.

Biosorption

Batch and rate equilibrium sorption studies were conducted with the three compounds expected to sorb most significantly onto activated sludge based on octanol/water partition coefficients—namely, 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and lindane. Results from sorption isotherm studies indicated a reasonably linear partitioning, and the rate studies demonstrated that equilibrium conditions occurred within approximately 15 min. A summary of biomass partition coefficients for the three compounds appears in Table 3.

Biodegradation

Completely mixed batch biodegradation rate studies were conducted with activated sludges from acclimated 10-L bioreactors to serve two purposes: 1) to confirm the biodegradation observed in 10-L CMF activated sludge units; and, 2) to measure pseudo first-order biodegradation rate coefficients for selected compounds. These studies were conducted under aerobic conditions without aeration to evaluate independently the removal mechanism of biodegradation. The full report details experimental procedures and results.

PAC Adsorption

Equilibrium adsorption isotherms were conducted with Hydrodarco C and each of the nine organic compounds in background solutions of bioreactor effluent. Results from these studies adhered to the Freundlich isotherm model, as shown by the data plotted in logarithmic form in Figure 2 for five of the compounds. The compounds could generally be ranked in the following decreasing order, based on the amount adsorbed for a given concentration of an equilibrium solution: 1,2,4-trichlorobenzene > lindane > 1,2-dichlorobenzene ≅ nitrobenzene > chlorobenzene ≅ ethylbenzene > o-xylene > toluene ≅ benzene. The full report contains results from additional isotherm studies.

Activated Sludge Bioreactor Studies

Activated sludge studies were conducted to fulfill three primary objectives:

1) To provide a reference point to which the results from bioreactor studies with carbon could be compared to evaluate the effect of carbon addition on the removal of the organic compounds;
2) To determine which of the organic compounds could be biodegraded by activated sludge under conditions representative of municipal activated sludge treatment; and,
3) To evaluate the relative importance of volatilization, biodegradation, and biosorption as removal mechanisms.

Table 1. *Physical Properties of Toxic Organic Compounds*

Compound	Solubility (mg/L)	Vapor Pressure (atm)	Henry's Constant (m^3atm/mol x 10^{-3})	Log Octanol/ Water Partition Coefficient
Purgeable:				
1. Benzene (BZ)	1750	0.125	5.49	1.95
2. Toluene (TL)	534	0.0374	6.66	2.69
3. Ethylbenzene (EB)	152	0.0125	8.73	3.15
4. o-Xylene (XL)	175	0.00868	5.27	3.12
5. Chlorobenzene (CB)	488	0.01382	3.71	2.84
Base Neutral Extractable:				
6. Dichlorobenzene (DB)	145	$1.32x10^{-3}$	2.96	3.38
7. 1,2,4-Trichlorobenzene (TB)	30	$5.53x10^{-4}$	2.32	4.26
8. Nitrobenzene (NB)	1900	$1.97x10^{-4}$	0.023	1.85
Pesticide:				
9. Lindane (LN)	7.3	$4.34x10^{-7}$	0.00043	3.72

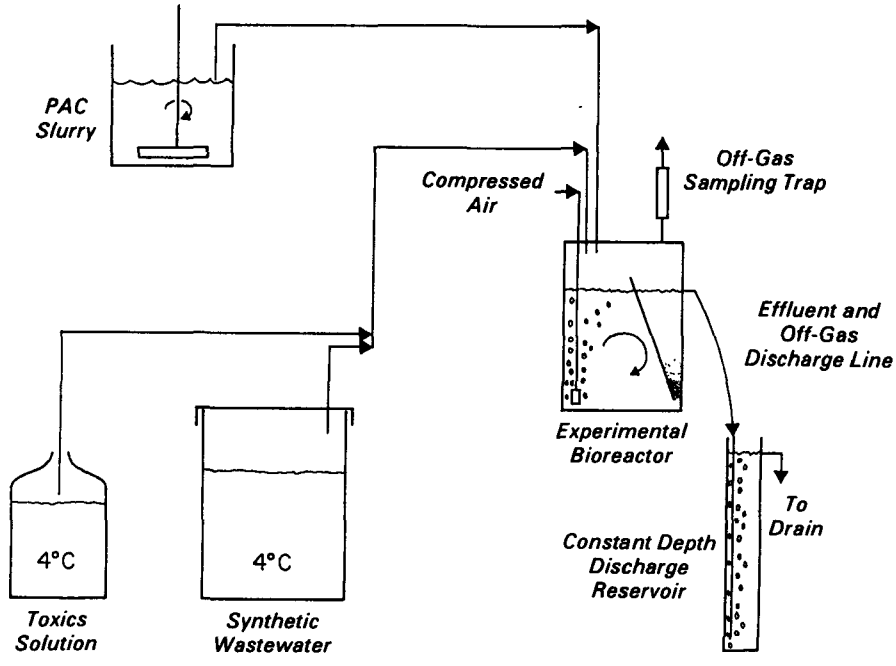

Figure 1. Schematic illustration of the experimental system.

Table 2. *Predicted and Measured Effluent and Off-Gas Concentrations From Bioreactors Without Activated Sludge*

Compound	Influent (μg/L)	Measured Effluent (μg/L)	Predicted Effluent (μg/L)	Measured Off-Gas (ng/L)	Predicted Off-Gas (ng/L)
Benzene	120	4.6	4.5	846	835
Toluene	122	4.5	4.1	784	786
Ethylbenzene	112	3.5	3.7	785	787
o-Xylene	112	5.2	5.4	796	764
Chlorobenzene	131	6.8	6.7	790	828
1,2-Dichlorobenzene	150	10.8	11.0	691	706
1,2,4-Trichlorobenzene	118	12.2	12.2	765	772

The 10-L bioreactors were initially seeded with activated sludge from the Ann Arbor wastewater treatment plant and operated in continuous flow mode with influents composed of synthetic wastewater and a specific organic solution. Influent concentrations of the specific compounds were typically maintained between 50 and 150 μg/L to simulate concentrations representative of those found in influents to full-scale municipal wastewater treatment facilities. Typical bioreactor operating conditions included a 6-hr hydraulic retention time, a 6-day solids retention time (SRT), a 3500-mg/L mixed liquor suspended solids (MLSS). Approximately 85% of influent total organic carbon (TOC) was removed.

Biological degradation of a toxic organic compound in the 10-L experimental bioreactors operated in continuous flow mode was evidenced by a significant difference between the mass fluxes into (influent) and out of (effluent, off-gas, and waste sludge) the bioreactors. Background studies conducted in the 10-L experimental bioreactors without activated sludge demonstrated that measured mass fluxes into and out of the bioreactors were nearly identical for both volatile and nonvolatile compounds. Values of N/N_0, the fractional recovery of a toxic compound, averaged between 0.93 and 1.00 when the bioreactors were operated without activated sludge. Thus, N/N_0 values greater than 0.90 were considered as complete recovery, and values less than 0.90 were interpreted as evidence of biological degradation.

Results from the activated sludge studies conducted in the 10-L CMF bioreactors with single organic solutes showed significant biodegradation of benzene, toluene, ethylbenzene, o-xylene, chlorobenzene

Table 3. *Biomass Partition Coefficients*

Compound	Log K_B*	Log K_{ow}+
1,2-Dichlorobenzene	*2.40*	*3.38*
Lindane	*2.75*	*3.72*
1,2,4-Trichlorobenzene	*3.01*	*4.26*

**Biomass partition coefficient.*
+Octanol/water partition coefficient.

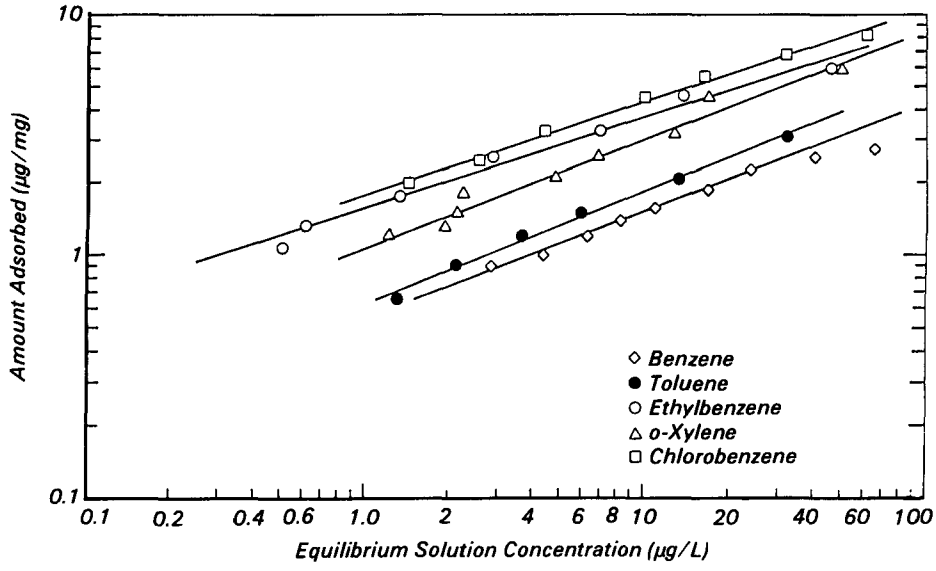

Figure 2. Experimental data and best-fit lines describing Freundlich adsorption isotherms for selected organic compounds from activated sludge bioreactor effluent by Hydrodarco C.

and nitrobenzene. Lindane and 1,2,4-trichlorobenzene were found to be nonbiodegradable, and 1,2-dichlorobenzene was poorly biodegraded. Table 4 summarizes the fate of each compound during activated sludge treatment in experimental bioreactors operated at 6-day SRT's under steady-state conditions. In general, biodegradation decreased as the degree of chlorination increased, as illustrated in Figure 3.

Results from activated sludge studies with benzene, a volatile and biodegradable compound, are presented in Figure 4 as an example of the results contained in the full report. A mass balance equation for a CMF reactor that incorporated the volatilization rate coefficients from the batch air-stripping studies was used to predict effluent and off-gas concentrations. Predicted and measured values showed good agreement for the nonbiodegradable compounds lindane and 1,2,4-trichlorobenzene. In the case of the biodegradable compounds such as benzene, the measured concentrations were significantly less than the predicted ones. Differences between predicted and measured values indicated that biodegradation effected reductions in both effluent and off-gas concentrations. Similar results were observed for all of the volatile, biodegradable compounds. The full report details results of studies designed to evaluate the influence on biodegradation of various bioreactor operating conditions (e.g., the influent concentration of a specific compound, non-steady-state addition of specific compounds to the influent, and SRT).

Integrated Activated Sludge and Carbon Treatment Studies

The effect of carbon addition on the removal of each organic compound was evaluated in 10-L bioreactors receiving slurried powdered carbon and operated in parallel with control-activated sludge units. Influent, effluent, and off-gas concentrations were measured every 2 to 4 days. Bioreactor operating conditions were similar to those previously described for the activated sludge studies.

Initial studies conducted with only one toxic compound added to a bioreactor influent were used to evaluate the effect of carbon dose on the removal of each compound. A summary of results from these studies appears in Table 5. The term "overall removal" in Table 5 is defined as the disappearance of a compound because of carbon adsorption or biodegradation or both. In general, the addition of carbon effected significant reductions in effluent and off-gas concentrations of the nonbiodegradable compounds lindane and 1,2,4-trichlorobenzene and of the poorly degraded compound 1,2-dichlorobenzene. The addition of carbon dosages from 50 to 100 mg/L did not have a significant effect on the steady-state effluent or off-gas concentrations of the biodegradable compounds benzene, toluene, ethylbenzene, o-xylene, chlorobenzene and nitrobenzene. To illustrate the types of results presented in the full report, Figures 5 and 6 compare results for benzene and 1,2,4-trichlorobenzene in bioreactor studies with 100-mg/L influent carbon dosages and in control-activated sludge studies.

The full report details results of additional studies designed to evaluate the effects of various operating conditions on

Table 4. *Fate of Toxic Organics in Acclimated Activated Sludge Bioreactors Operated at 6-Day SRT's Under Steady-State Conditions*

	Percent of Influent			
Compound	Effluent	Off-Gas	Biosorbed	Biodegraded
Nitrobenzene	*2*	*<1*	*0*	*98*
Benzene	*<1*	*16*	*0*	*84*
Toluene	*<1*	*17*	*0*	*83*
Ethylbenzene	*<1*	*22*	*0*	*78*
o-Xylene	*<1*	*25*	*0*	*75*
Chlorobenzene	*<1*	*20*	*0*	*80*
1,2-Dichlorobenzene	*6*	*59*	*0*	*35*
1,2,4-Trichlorobenzene	*10*	*90*	*<1*	*0*
Lindane	*93*	*0*	*7*	*0*

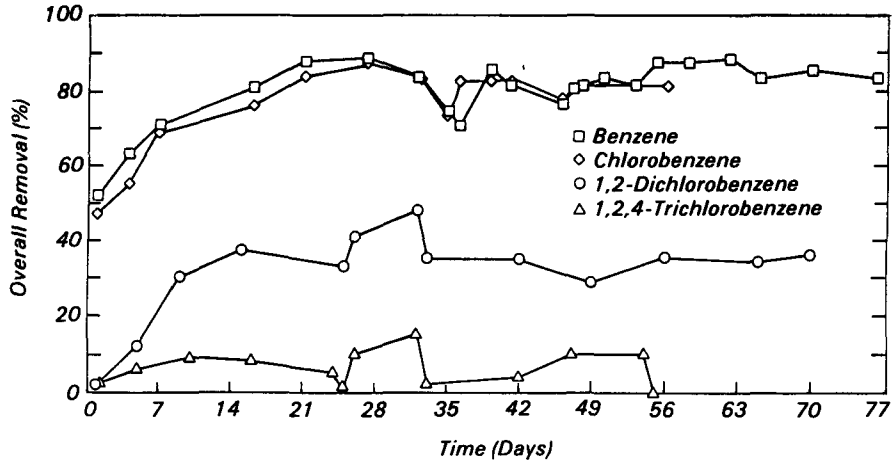

Figure 3. Effect of increased chlorination on the biodegradation (overall removal) of volatile organic compounds during single-solute activated sludge studies.

the removal of toxic organic compounds in activated sludge systems receiving PAC.

Conclusions

This project provides information on the potential for conventional activated sludge systems to effect significant biodegradation of trace concentrations of organic pollutants. The study also demonstrates that the addition of activated carbon to activated sludge systems can be an effective technique for providing enhanced removal of nonbiodegradable and poorly biodegradable compounds. Major conclusions that can be drawn from the study are as follows:

- Benzene, toluene, ethylbenzene, o-xylene, chlorobenzene, and nitrobenzene are effectively biodegraded in activated sludge systems;
- Carbon dosages of 100 mg/L had no significant effect on the steady-state effluent and off-gas concentrations of the biodegradable compounds;
- 1,2-Dichlorobenzene, 1,2,4-trichlorobenzene, and lindane are not effectively removed during activated sludge treatment;
- Carbon dosages of 25 to 50 mg/L effected 80% to 95% removal of 1,2-dichlorobenzene, 1,2,4-trichlorobenzene, and lindane;
- Addition of carbon resulted in approximately equal percent reductions in both effluent and off-gas concentrations of volatile compounds; and,
- The overall removal of nonbiodegradable compounds under steady-state operating conditions was a function of the influent carbon dosage and not of the mixed liquor concentration of carbon.

The full report was submitted in fulfillment of Grant No. CR 806030 by the University of Michigan under the sponsorship of the U.S. Environmental Protection Agency.

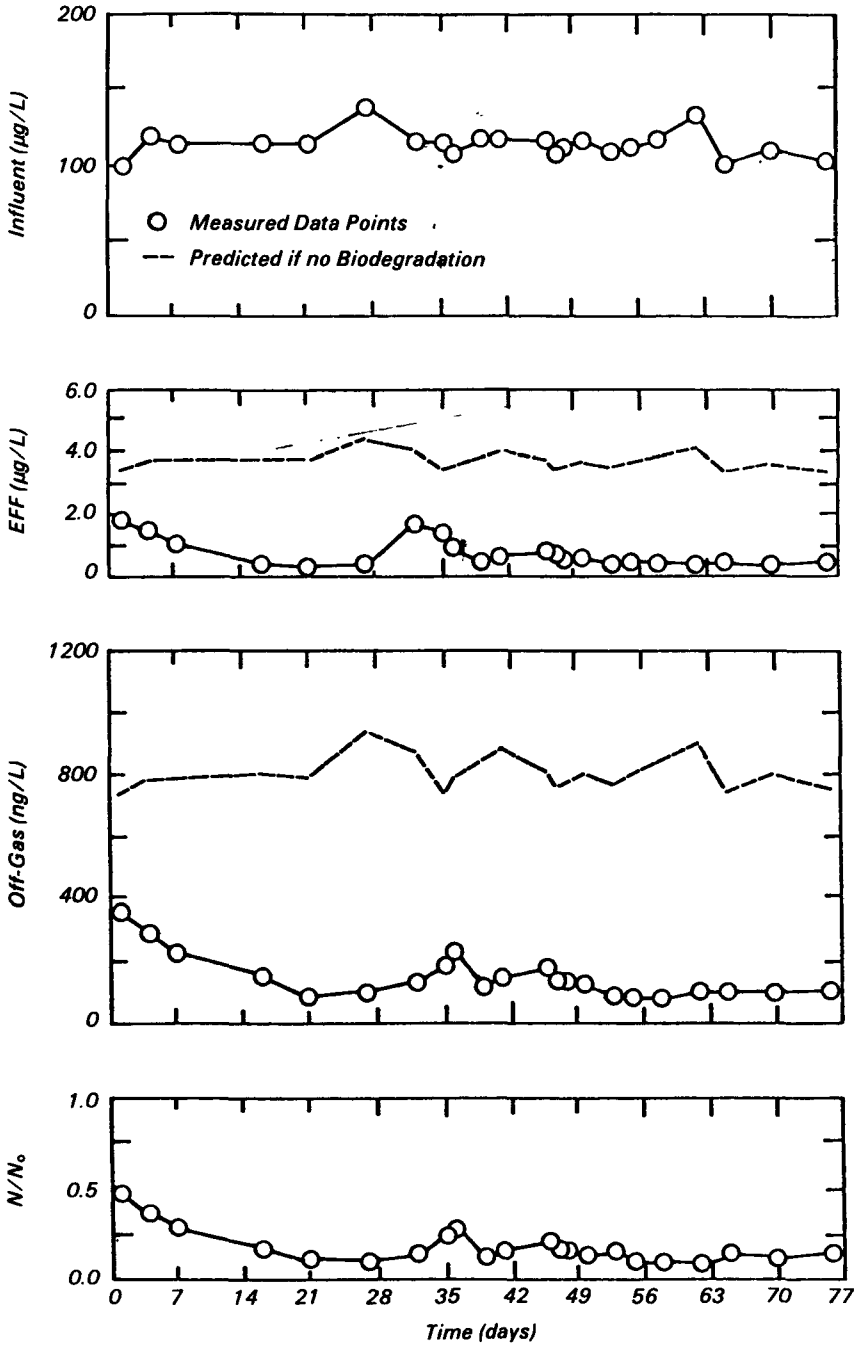

Figure 4. *Benzene influent, effluent, and off-gas concentrations and fractional recoveries, N/N_o measured during a 6-day SRT activated sludge study. (Dashed lines give values predicted by air-stripping, assuming no biodegradation.)*

Table 5. *Overall Percent Removals Measured at Various Influent Carbon Dosages**

Compound	Control	Carbon Dosage 12.5 mg/L	25 mg/L	50 mg/L	100 mg/L	200 mg/L
Biodegradable:						
Benzene	83	ND+	79	84	86	86
Toluene	84	ND	ND	ND	ND	90
Ethylbenzene	81	ND	79	85	87	87
o-Xylene	78	ND	ND	82	ND	ND
Chlorobenzene	82	ND	82	85	90	90
Nitrobenzene	97	ND	ND	97	99	ND
Poorly Biodegradable:						
1,2-Dichlorobenzene	36	ND	61	71	93	94
Nonbiodegradable:						
1,2,4-Trichlorobenzene	0	ND	69	77	94	94
Lindane	0	68	84	92	ND	ND

*Overall Removal = $(1-N/N_o) \times 100$
N_o = influent flux
N = sum of effluent and off-gas fluxes
+ND = Not Determined

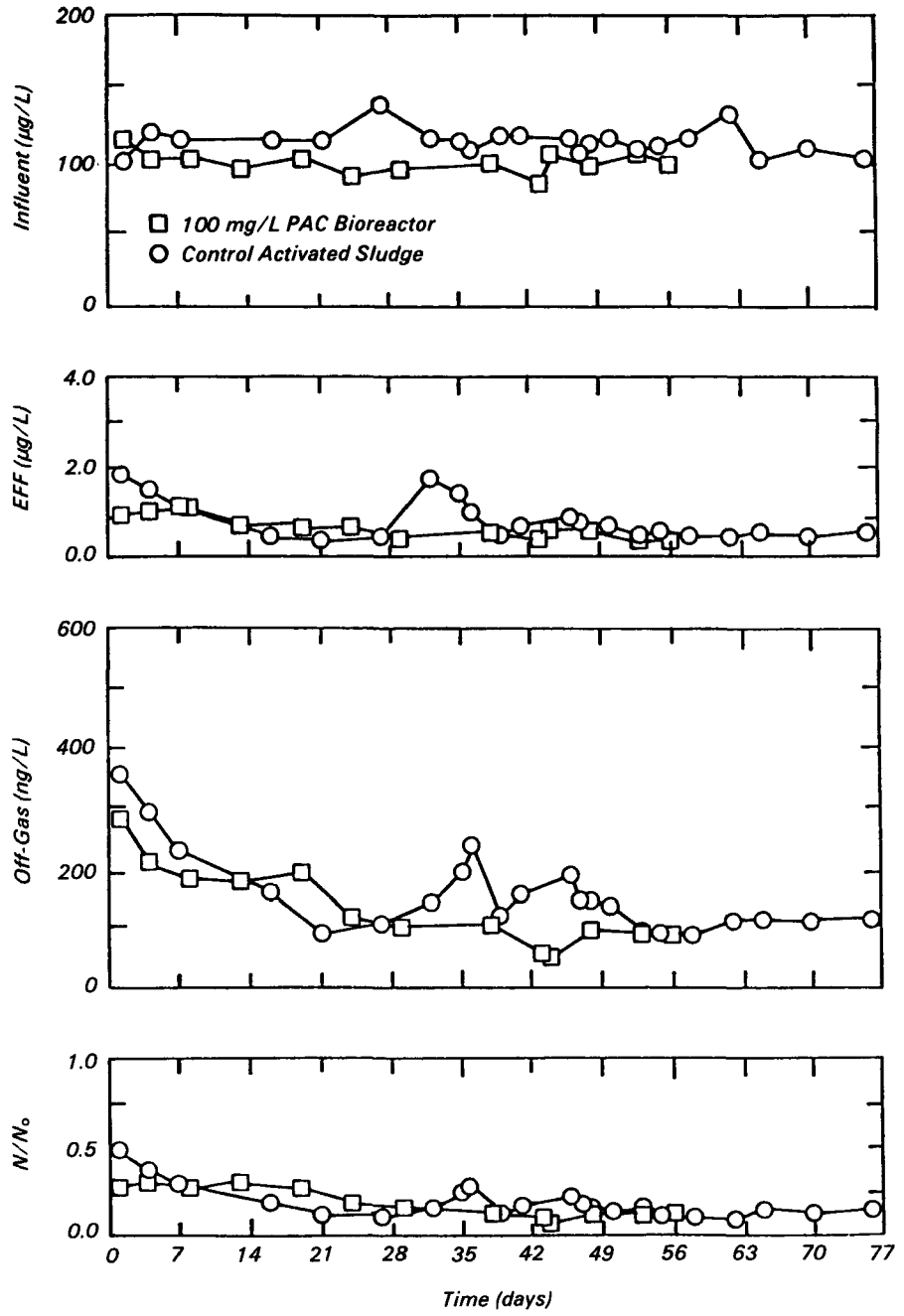

Figure 5. *Effect of a 100-mg/L influent PAC dose of Hydrodarco C on benzene effluent and off-gas concentrations and fractional recoveries, N/N_o.*

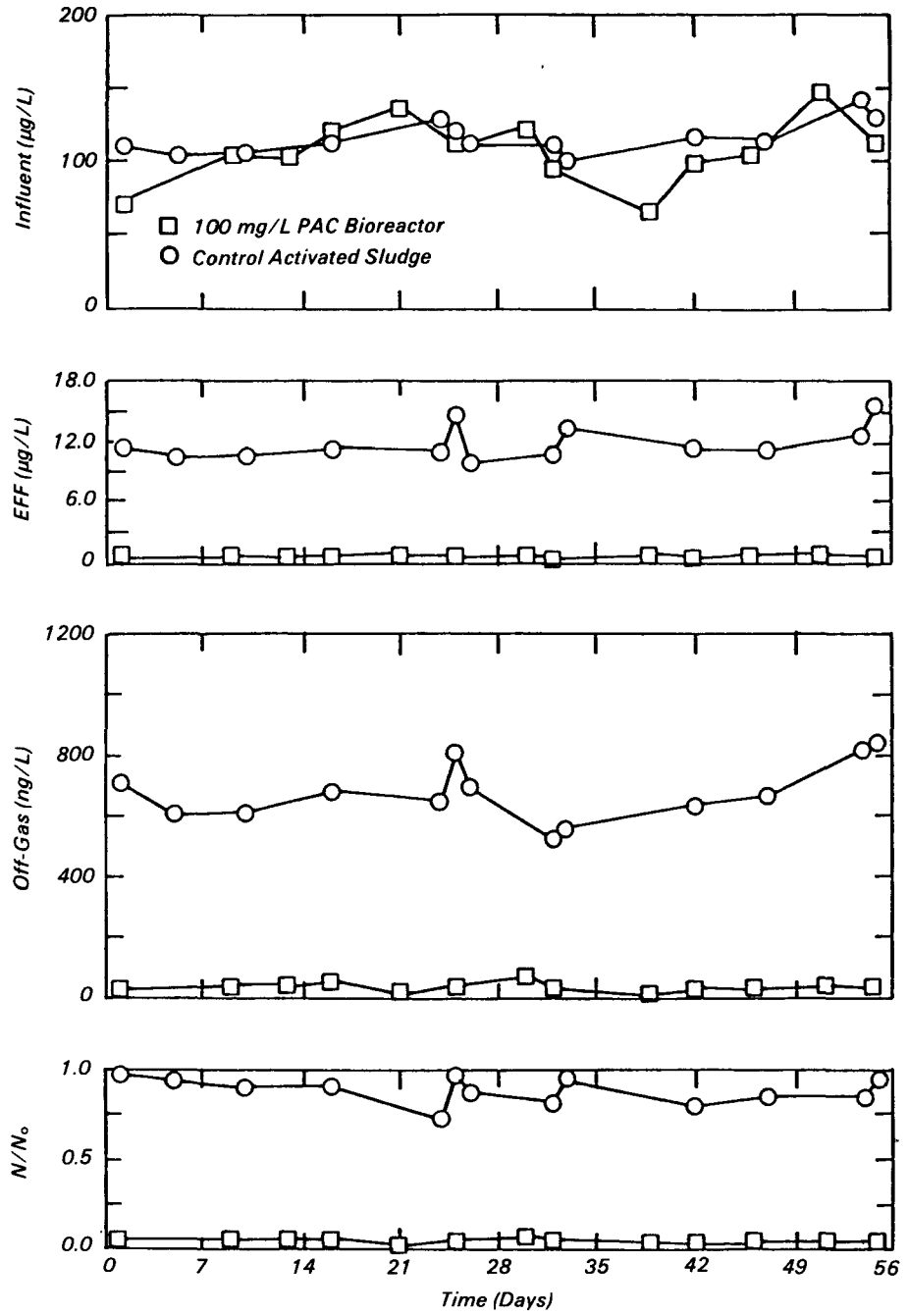

Figure 6. *Effect of a 100-mg/L influent PAC dose of Hydrodarco C on 1,2,4-trichlorobenzene effluent and off-gas concentrations and fractional recoveries, N/N_o.*

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***Sidney A. Hannah** is the EPA Project Officer (see below).*
The complete report, entitled "Toxic Substance Removal in Activated Sludge and PAC Treatment Systems," (Order No. PB 86-182 425/AS; Cost: $40.95, subject to change) will be available only from:
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