JV TASK 15 – POWDERED ACTIVATED CARBON FROM NORTH DAKOTA LIGNITE: AN OPTION FOR DISINFECTION BY-PRODUCT CONTROL IN WATER TREATMENT PLANTS

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TABLE OF CONTENTS

LIST OF TABLES

POWDERED ACTIVATED CARBON FROM NORTH DAKOTA LIGNITE: AN OPTION FOR DISINFECTION BY-PRODUCT CONTROL IN WATER TREATMENT PLANTS

EXECUTIVE SUMMARY

New federal drinking water regulations have been promulgated to restrict the levels of disinfection by-products (DBPs) in finished public water supplies. DBPs are suspected carcinogens and are formed when organic material is partially oxidized by disinfectants commonly used in the water treatment industry. Additional federal mandates are expected in the near future that will further affect public water suppliers with respect to DBPs.

Powdered activated carbon (PAC) has traditionally been used by the water treatment industry for the removal of compounds contributing to taste and odor problems. PAC also has the potential to remove naturally occurring organic matter (NOM) from raw waters prior to disinfection, thus controlling the formation of regulated DBPs. Many small water systems are currently using PAC for taste and odor control and have the potential to use PAC for controlling DBPs.

This project, a cooperative effort between the Energy & Environmental Research Center (EERC), the Grand Forks Water Treatment Plant, and the University of North Dakota Department of Civil Engineering, consists of several interrelated tasks. The objective of the research was to evaluate a cost-effective PAC produced from North Dakota lignite for removing NOM from water and reducing trihalomethane formation potential. The research approach was to develop a statistically valid testing protocol that can be used to compare dose–response relationships between North Dakota lignite-derived PAC and commercially available PAC products. A statistical analysis was performed to determine whether significant correlations exist between operating conditions, water properties, PAC properties, and dose–response behavior. Pertinent physical and chemical properties were also measured for each of the waters and each of the PACs.

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1.0 INTRODUCTION AND BACKGROUND

The U.S. Environmental Protection Agency (EPA), through the 1996 Safe Drinking Water Act Amendments, has promulgated regulations that limit the levels of disinfection by-products (DBPs) in drinking water (U.S. Environmental Protection Agency, 1998). DBPs are formed when naturally occurring organic matter (NOM) reacts with specific disinfectants, e.g., chlorine, chloramines, and chlorine dioxide. Regulated compounds and maximum contaminant levels (MCLs) under the Stage 1 Disinfectants/Disinfection By-Products Rule (D/DBPR), which was published in December 1998, are shown in Table 1. Compliance dates are January 2002 for large (>10,000 customers) surface water systems and January 2004 for small surface water and all groundwater systems. The D/DBPR also mandates a maximum residual disinfectant level of 4.0 mg/L for chlorine and chloramines and 0.8 mg/L for chlorine dioxide.

TABLE 1

Regulated DBPs and Associated MCLs

Regulated DBP	MCL, mg/L
Total Trihalomethanes, TTHM[1]	0.08
Haloacetic Acids, HAA5[2]	0.06
Chlorite	1.0
Bromate	0.01

[1] Sum of chloroform, bromodichloromethane, dibromochloromethane, and bromoform

[2] Sum of mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids.

These new federal drinking water regulations may require public water suppliers to adjust treatment practices or incorporate additional treatment operations into their existing treatment trains. Many options have been identified, including membrane processes, granular activated carbon, PAC, enhanced coagulation and/or softening, and alternative disinfectants (e.g., chlorine dioxide, ozone, and chloramines). Of the processes being considered, PAC appears to offer an attractive benefit-to-cost advantage for many water treatment plants, particularly small systems (those serving fewer than 10,000 customers).

A key component in the formation of DBPs is the mandated CT requirements to ensure a given pathogen kill, where C is the residual disinfectant concentration (mg/L) and T is the time (in minutes) that water is in contact with the disinfectant. Tables are available that relate CT values to levels of inactivation under various operating conditions. Different tables exist for different disinfectants. As the CT value is increased, a greater percentage of microorganisms are inactivated by chemical disinfection. The CT, and therefore the level of inactivation, can be increased by applying greater doses of the disinfectant or by increasing the time that the water is in contact with the disinfectant. However, increased CT can also result in increased DBP formation. Removal of NOM in upstream treatment operations through the use of PAC would allow for longer disinfectant CT by decreasing the concentration of precursors that contribute to the formation of DBPs.

The allowable levels of TTHM in drinking water are currently regulated by federally mandated standards for public water suppliers serving more than 10,000 customers. The Stage 1 DBPR will establish the levels of acceptable DBPs in finished drinking water supplies to those shown in Table 1. Proposed changes to these standards (e.g., Stage 2 DBPR) are expected to further restrict allowable DBP levels. The task of meeting these new standards will raise production costs significantly for many treatment plants. Small treatment plants will be particularly affected because they have relatively small customer bases to absorb cost increases.

A major advantage of using PAC for removal of NOM during water treatment is that it requires a relatively small cost expenditure to set up a PAC system compared to other process alternatives. In fact, many plants are currently using PAC for control of taste and odors and, therefore, already have a PAC storage and feed system in place. PAC can be added to the water at a number of different points in the treatment process, thus allowing some flexibility in the mode of operation. PAC can be used intermittently, as needed, during periods of high THM formation potential which reduces treatment costs.

The main cost associated with the use of a PAC system to remove NOM from water is the cost of the PAC itself. In order to get the greatest cost benefit from the system, care must be taken to select the best PAC product for use in the plant. Several factors can impact the selection of a PAC, including the site-specific performance of the PAC for reduction of taste and odor, reduction of NOM and THM formation potential, the cost of the PAC, and the ease of feeding the material.

Several research projects have reported on procedures useful for selecting specific types of PAC for removal of organics from water. Papers by personnel from the Manatee County, Florida, water treatment plant discuss work done to develop performance-based bid specifications for PAC (McLeod and others, 1993; McLeod and Simpson, 1993). The objective in these studies was to remove odor-causing organics. The following conclusions were drawn from these papers:

- The commonly used PAC adsorption indices and physical properties did not generally correlate with PAC performance.

- The tannin value was the best indicator of PAC performance, and an inverse relationship existed between tannin value and odorant removal.

- The initial odorant concentration had no effect on percent odorant removal.

- The presence of NOM decreased adsorption of odorants.

- A four-stage procedure involving development of dose–response curves, establishment of performance goals, calculation of dose–equivalent factors, and application of these factors to bid prices was an effective means of writing bid specifications for PAC.

- Other factors such as compatibility with other chemicals, handling, operator safety, treatment residual considerations, and delivery limitations should also be considered for effective bid specifications.

Research by personnel from the City of Edmonton, Alberta, water treatment plant studied removal of odor, color, dissolved organic carbon (DOC), and gasoline from water (Gammie and others, 1992). Although this work had a broader scope than the work done at the Manatee plant, many of the conclusions were similar. The following conclusions were drawn from this work:

- Carbon performance and ranking were not related to cost or to standard tests such as iodine number or phenol value.

- The "best" carbons performed well for removal of all parameters, thus different carbons are not needed for different organics events.

- Carbon ranking bore some relation to tannin values.

- Accumulation of PAC in an upflow clarifier, while resulting in high concentrations of PAC in the sludge, did not measurably improve removals.

- Removals and ranking of activated carbons may vary with water source and the types of organics; water plants should evaluate carbons on the raw water that they are treating for the parameters to be removed.

The projects conducted in Manatee and Edmonton both involved development of dose–response curves for a number of different PACs treating a site-specific water. This approach seemed to be sound and yielded useful information for a specific site. The usefulness of these studies is limited by the fact that in each case only one water was tested, making it impossible to draw conclusions about whether results obtained for one water type can be extended to other waters. The research detailed in this report evaluated five different waters, with an attempt to draw correlations between water characteristics and PAC performance. Ideally, these correlations would allow smaller water treatment plants to select a cost-effective PAC for their own use without doing extensive testing and analyses.

Further, the studies done in Manatee and Edmonton did not vary major operational parameters such as water temperature and PAC contact time in their test plans. It is possible that these parameters could significantly impact appropriate PAC dose and so should be varied in the evaluation procedure. Thus water temperature and CT were included as variables in the testing matrix designed for the proposed research and, hence, are indirectly involved with the PAC dose–response relationship.

2.0 OBJECTIVES

The overall objectives of this study were to evaluate the use of a PAC product prepared from a North Dakota lignite for removing NOM from water as a means of controlling DBP formation during drinking water treatment. The project consisted of several interrelated tasks including 1) preparation of PAC from North Dakota lignite, 2) collection and characterization of waters and commercial PACs, 3) adsorption testing using a matrix test design, and 4) statistical analysis of adsorption test data.

3.0 RESULTS

3.1 Preparation of PAC from North Dakota Lignite

Current literature describes the pore-volume distribution in lignite-based activated carbons as low in micropore volume (17% of the distribution) and high in concentration of macropores (35%–50%) (Bansal, 1988; Wilson, 1981). Although the pore structure of the original lignite shows considerable micropores, these are "burned out" in the charring and activation process, because of the high volatility and reactivity of the lignite. Mass transfer within the carbon is slow for sorption in aqueous systems; thus a higher proportion of larger pores is desired for distribution of solute to the sorbent surfaces. Therefore, the lignite-derived carbons with the larger meso- and macropore distributions are more appropriate for adsorption from the liquid phase. Since the goal is to remove large NOM (humates) from water, carbons with a larger meso- and macropore distribution are better suited to facilitate sorption of the very large humate molecules that will not fit into the micropores. For gas treatment applications, the lignite-based carbons are at a severe disadvantage because of their low concentration of micropores.

Rist and Harrison (1985) reported that the pore-size distribution of Darco (Texas lignite-based) carbon was bimodal, but with substantial pore sizes of 22 and 75 Å. Samples of Louisiana lignite-based carbons had mostly the 20-Å pores, but in this set of carbons, the total surface area and the total pore volumes were low (20%–40% of the Darco carbon). Since the Louisiana lignites are highly aliphatic, they give a much different pore distribution when activated. No similar pore characterization exists for the highly aromatic North Dakota lignites, but they should produce carbons similar to those derived from Texas lignite.

Removal of mineral matter from the precursor lignite has recently been shown to improve the micropore volume of the activated carbon (Samaras and others, 1994). The reason for this is that the mineral matter catalyzes the pyrolysis and carbonization reactions that gasify the char and enlarge the pores. Thus lowering the activity of the char slows down the loss and allows the microporosity to develop. Earlier, Mochida and coworkers (1984) demineralized Metla coal and improved the carbonization (decreased isotropic area). Our recent studies with acid-extracted leonardite demonstrated that higher adsorptive capacity was achieved with an acid-treated leonardite.

Not only does the mineral content of the coal significantly affect the pore structure of the subsequent carbon, but it can also significantly affect the chemical factors that are important in sorption. Large concentrations of divalent cations in the carbon sorbent could promote binding to the negatively charged humate macromolecules in the water. It is, therefore, very important to adequately characterize the structures and inorganic contents of the lignites that are carbonized in this study and to correlate these properties with the pore distributions, surface areas, and sorption activities of the carbons prepared from the various lignites.

Carbonization/activation experiments were performed on two lignites from North Dakota and the results compared with those obtained in similar tests with commercial activated carbons prepared from other materials. Lignite samples were collected from the Knife River Coal Company and the Dakota Gasification Company (Freedom Mine). The original intent was to collect samples of both high-sodium and high-calcium mineral content. Preliminary testing, however, indicated that the high-calcium samples were not as effective in removing humates from water. Therefore, continued testing was conducted using only the high-sodium-content lignites.

Bench-scale carbonization/activation was conducted with 100–150-g samples that were dried in an oven at 100°C under nitrogen. The lignite samples were heated to 400°C in a tube furnace until evolution of tars ceased. The char was then heated to 750°C, and steam (in nitrogen) was passed through the char for activation. Yields of activated carbon were generally about 35%–40%.

3.2 Collection and Characterization of Waters and PACs

Five different source waters and five different PACs were used in this study. The five waters used in the test program included surface waters collected from the Red Lake River at East Grand Forks, Minnesota, the Park River at Grafton, North Dakota, the Missouri River at Mandan, North Dakota, the Red River of the North at Grand Forks, North Dakota, and the Mississippi River at St. Cloud, Minnesota. With the exception of the Red Lake River sample, which was collected on several different occasions at the beginning of the study, bulk river water samples were collected in 55-gallon polyethylene barrels and stored at 4°C until used in sorption testing.

These waters were all analyzed for general water quality parameters, including pH, temperature, turbidity, conductivity, alkalinity, hardness, DOC, TTHM, and THM formation potential. Selected results of these analyses are shown in Table 2.

As mentioned previously, two North Dakota lignite-derived PACs were produced on the bench scale for DOC sorption testing, each produced from high-sodium lignite feedstocks. Three additional commercially available PACs were also selected for testing and were chosen to represent a cross section of carbons from feedstocks typically used for activated carbon production. The commercial PACs included Darco Norit, produced from Texas lignite; Acticarb, an activated carbon produced from coconut husks; and Cal-Pacific, a wood-based PAC.

As previously reported (McLeod and others, 1993), commonly used PAC adsorption indices do not generally correlate with PAC performance, and carbon cost rankings were not related to standard tests such as iodine number or phenol value (Gammie and others, 1992). Therefore, rather than develop values for standard adsorption indices, single-point adsorption tests were used to compare carbon effectiveness. The single-point sorption indicators included methylene blue (cationic charge), methyl red (anion charge), and a humate (anionic charge) that was developed to simulate NOM that is contributed by peat which is common to waters of the region. These sorption tests were used to define conditions for PAC production from the North Dakota lignites and compared to a commercial PAC produced from a Texas lignite (Darco), a product known to have high sorption capacities for naturally occurring organics. A PAC dose of 200 mg/L was used in each of the tests which were conducted at room temperature. Results of the single-point sorption tests are listed in Table 3. These preliminary results showed the North Dakota lignite-derived PACs to compare very favorably to the commercial PAC produced from the Texas lignite.

TABLE 2

Raw Water Quality Parameters

Source Water	pH	Conductivity, µS/cm	Alkalinity, mg/L	Hardness, mg/L	DOC, mg/L	UV-254	THMfp, µg/L
Red Lake River	8.0	412	179	223	14.3	22.6	441
Missouri River	8.0	595	144	194	4.2	4.5	109
Park River	8.1	1760	268	522	11.3	11.7	372
Mississippi River	8.2	81	151	160	11.2	18.8	464
Red River	8.5	642	268	306	11.5	15.2	506

TABLE 3

Single-Point Sorption Capacity Comparison

Substrate	PAC	Sorption, mg/g
Methylene Blue, 200 mg/L	Knife River	98
	Darco	92
Methyl Red, 200 mg/L	Freedom	48
	Knife River	58
	Darco	59
Humic Acid, 100 mg/L	Freedom	134
	Knife River	138
	Darco	138

3.3 Adsorption Testing

Two-hundred and fifty individual tests were performed, 50 for each source water, during adsorption testing. Each water was subjected to a statistically valid testing protocol designed to relate removal of NOM and reduction of THM formation potential to PAC dose, contact time, and water temperature. A factorial design for three variables was used for the test matrix. This approach required testing three preset levels for each independent variable. The values used for the independent variables, shown in Table 4, were selected to represent the range of water temperatures with varying seasons for a variety of water treatment plant sizes. The test matrix contains nine different sets of conditions, with a replication of center-point conditions (see Table 5). The low value for the variable is indicated with a − 1, the center-point value is indicated with a 0, and the high value is indicated with a +1 in the matrix. This testing matrix was used for each source water–PAC combination. NOM reduction was determined by the DOC concentrations of the water before and after the adsorption test.

TABLE 4

Statistical Matrix Test Variables

	− 1	0	+1
PAC Dose, mg/L	5	52.5	100
Temperature, °C	5	15	25
Contact Time, minutes	20	70	120

TABLE 5

2^3 Factorial Test Matrix

Test Number	PAC Concentration	Contact Time	Water Temperature
1	− 1	− 1	− 1
2	+1	− 1	− 1
3	+1	+1	− 1
4	+1	+1	+1
5	0	0	0
6	+1	− 1	+1
7	− 1	− 1	+1
8	− 1	+1	+1
9	− 1	+1	− 1
10	0	0	0

The sorption tests were conducted using a variable-speed, six-paddle laboratory gang stirrer placed in an insulated water bath to control sample temperature. The source waters were allowed to reach the desired operating temperature. PAC was carefully measured and added to the respective beakers, and 1000 mL of source water was added. The samples were subjected to a rapid mix at 80 rpm for 5 minutes, and the speed was gradually reduced to 40 rpm which was maintained for the duration of the contact periods. The samples were then filtered through a 0.45-µm filter and analyzed for DOC, UV absorption, and THMfp analyses.

Within a reasonable amount of analytical error, the analytical results were acceptable on all but the Red River of the North water samples. These samples showed an increase in DOC after treatment. This was coincident with repairs that were conducted on the total organic carbon (TOC) analyzer. Attempts were made to remedy the problem, but it appeared that the analyzer did not entirely purge the previous sample before measuring the next sample. An investigation was conducted to develop a possible correlation between UV absorption and DOC, but no significant correlation was found. THMfp data were not compared because the acceptable range of error for that analysis is ± 30% and not within an 85% confidence interval. Therefore, DOC results for the Red River of the North were excluded from subsequent statistical analyses.

3.4 Statistical Analysis of Adsorption Test Data

The use of full-factorial experimental matrices permitted the results to be analyzed using regression analysis. During a regression analysis, the degree of effect of all independent variables (in this case, the operating parameters) and their combinations on the dependent variable (i.e., the DOC reduction) is determined. A SAS™ statistical analysis software package was used to determine the effect of PAC concentration, time, and temperature on DOC reduction for each water–carbon combination. Both backwards elimination and stepwise regression analyses were performed. When performing a backwards elimination procedure, the independent variable having the least (statistically) significant effect on the dependent variable is dropped. The procedure is repeated until the remaining independent variables are all considered to significantly affect the dependent variable. The stepwise procedure is the reverse of the backwards elimination procedure, in that independent variables are added until one is found not to be statistically significant. The result of a regression analysis is a mathematical equation (or model) that describes the combined effect of the independent variables on the dependent variable. All of the models determined during these regression analyses fit the data at an 85% confidence interval.

Independent variables are entered into a regression analysis in coded form so that the coded value of each variable is either −1, 0, or 1. Coded values are based on upper and lower variable ranges as well as the average (or center point) value for that variable. The ranges and center points used to code each operating parameter are presented in Table 6. The models resulting from the regression analyses are listed in Table 7. It should be noted that the models include coded values of each variable. For example, a DOC reduction for the Mississippi River water–Knife River PAC combination when a particular PAC concentration is used cannot be determined by plugging that concentration value into the listed model. Rather, the **coded** concentration value must be inserted into the model.

TABLE 6

Coded Values for Operating Parameters

Parameter	Valid Range	Center Point	Code Definition
PAC Concentration	5–100 mg/L	52.5 mg/L	(Conc.–52.5)/47.5
Time	20–120 min	70 min	(Time–70)/50
Temperature	5°–25°C	15°C	(Temp.–15)/10

Spreadsheets were constructed for the DOC reduction expected for each water–PAC combination as follows. Values of the operating parameters were input over their ranges and the DOC reduction calculated using the mathematical models derived during the statistical analysis. The DOC reductions were plotted to show the values at various operating conditions that were not actually tested. The actual data also were plotted on their corresponding predictive plots. All of the plots are contained in Appendix A.

The plots in Appendix A illustrate graphically the response of DOC reduction according to the model equations. These results have been summarized according to considerations for waters and PAC in Sections 3.4.1 and 3.4.2, respectively.

3.4.1 Waters

3.4.1.1 Red Lake River Water

The greatest predicted DOC reduction for Red Lake River water was about 30%. This was predicted for an Acticarb PAC dose of 100 mg/L, a temperature of 5°C, and a contact time of 120 min. The relationship between Red Lake River water and Acticarb sorbent is complex, depending on PAC concentration, time, and temperature. A similar relationship exists between Red Lake River water and Freedom PAC. This combination resulted in a predicted DOC removal of about 21% at a loading of 100 mg PAC/L and a contact time of 20 min at 25°C. In contrast, the only variable of those statistically evaluated which significantly affected DOC reduction was PAC concentration for the Knife River and Darco Norit PACs. The maximum DOC removal using Darco Norit PAC was approximately 17% at a PAC concentration of 100 mg/L. However, the Knife River PAC–Red Lake River water model did not predict any DOC removal. The Cal-Pacific PAC DOC removal data could not be reduced to a valid model that met the 85% confidence interval criterion for Red Lake River water.

TABLE 7

Descriptive Models for Each Water–Activated Carbon Combination

Water	PAC	Model
Missouri River	Acticarb	DOC reduction = −0.099 − (0.075 × coded conc.) + (0.142 × coded temp.)
	Cal-Pacific	No model met the 85% confidence criterion
	Knife River	DOC reduction = 0.0889 − (0.126125 × coded time) + (0.130875 × coded temp.)
	Freedom	DOC reduction = 0.0462 − (0.119125 × coded conc.) − (0.054125 × coded time) + (0.182375 × coded temp.) + (0.082125 × coded conc. × coded temp.) − (0.065125 × coded conc. × coded time × coded temp.)
	Darco Norit	DOC reduction = 0.1025 − (0.0775 × coded time) + (0.3165 × coded temp.) + (0.1475 × coded conc. × coded temp.)
Park River	Acticarb	DOC reduction = 0.1808 − (0.146 × coded time) + (0.083 × coded temp.) + (0.109 × coded time × coded temp.)
	Cal-Pacific	DOC reduction = 0.1595 − (0.086625 × coded time) + (0.052125 × coded time × coded temp.)
	Knife River	DOC reduction = 0.2567 + (0.05475 × coded conc.) − (0.04825 × coded time) + (0.03525 × coded temp.) − (0.054 × coded conc. × coded temp.) + (0.0565 × coded time × coded temp.)
	Freedom	DOC reduction = 0.2515 − (0.05125 × coded time) − (0.07 × coded conc. × coded temp.)
	Darco Norit	DOC reduction = 0.2786 + (0.09275 × coded conc.) − (0.07 × coded time) − (0.06825 × coded conc. × coded temp.)
Red Lake River	Acticarb	DOC reduction = −0.0061 + (0.087 × coded conc.) − (0.04825 × coded temp.) − (0.05775 × coded conc. × coded temp.) − (0.1125 × coded time × coded temp.)
	Cal-Pacific	No model met the 85% confidence criterion
	Knife River	DOC reduction = −0.1797 + (0.11025 × coded conc.)
	Freedom	DOC reduction = 0.0406 + (0.160625 × coded conc.) − (0.082625 × coded time × coded temp.) + (0.076375 × coded conc. × coded time × coded temp.)
	Darco Norit	DOC reduction = 0.081 + (0.09225 × coded conc.)
Mississippi River	Acticarb	DOC reduction = 0.0466 + (0.125375 × coded conc.) + (0.022625 × coded time)
	Cal-Pacific	DOC reduction = −0.0387 + (0.051625 × coded conc.) + (0.035625 × coded conc. × coded temp.)
	Knife River	DOC reduction = 0.0591 + (0.145125 × coded conc.)
	Freedom	DOC reduction = 0.05266667 + (0.13325 × coded conc.) + (0.0195 × coded conc. × coded temp.)
	Darco Norit	DOC reduction = 0.0828 + (0.176 × coded conc.) + (0.0215 × coded time) − (0.02575 × coded temp.) + (0.01925 × coded conc. × coded temp.)

3.4.1.2 Park River Water

All of the PACs removed DOC from Park River water. The greatest reduction was predicted to be >50% using Darco Norit PAC at a dose of 100 mg/L at 5 °C and a 20-min contact time. The Park River water–Darco Norit PAC relationship is affected by PAC concentration, time, and temperature. This is the case with the Knife River and Freedom PACs as well. The predicted maximum DOC reductions for Knife River and Freedom PACs are nominally 48% and 39%, respectively, at PAC concentrations of 100 mg/L. The DOC-reducing abilities of both Acticarb and Cal-Pacific depend on time and temperature but not on PAC concentration. The maximum DOC reduction predicted for Acticarb with Park River water is about 39% at 5 °C and a 20-min contact time. Cal-Pacific PAC is predicted to remove about 33% of the DOC from Park River water at the same conditions. It should be noted that the greatest DOC reduction for Park River water is predicted to occur at the same temperature, contact time, and PAC loading (5 °C, 20 min, and 100 mg/L) for all five PACs.

3.4.1.3 Mississippi River Water

The highest degree of DOC removal predicted for Mississippi River water is 29% with Darco Norit PAC at a concentration of 100 mg/L and at 5 °C. Although the DOC reduction achieved by Darco Norit PAC from Mississippi River water depends on time, temperature, and PAC concentration, the most effective predicted conditions are relatively time-independent. The DOC reduction achieved by Acticarb PAC depends on contact time and PAC concentration, with the maximum predicted to be slightly less than 20% at a PAC concentration of 100 mg/L and a contact time of 120 min. The models for the Cal-Pacific and Freedom PACs include concentration and temperature, with the greatest DOC reduction predicted to be 5% for Cal-Pacific and 21% for Freedom PAC. These reductions are both predicted for PAC concentrations of 100 mg/L and temperatures of 25 °C. A maximum DOC reduction of 21% is predicted for Knife River PAC at a concentration of 100 mg/L. Neither time nor temperature factor into the DOC reduction achieved by Knife River PAC with this water.

3.4.1.4 Missouri River Water

The maximum DOC reduction from Missouri River water was predicted to be >50%, achieved using Darco Norit PAC at a concentration of 100 mg/L, a temperature of 25 °C, and a contact time of 120 min. The model for removal of DOC from Missouri River water using Darco Norit was shown to be dependent on temperature, time, and PAC concentration. This is also the case with Freedom PAC, where a maximum 30% DOC reduction occurs at a PAC concentration of 100 mg/L, a temperature of 25 °C, and a contact time of 20 min. The DOC reduction achieved by Knife River PAC depends only on time and temperature; a maximum DOC reduction of 34% was predicted to occur at a contact time of 20 min and a temperature of 25 °C. The greatest DOC reduction predicted for Acticarb PAC is 32% at 25 °C and a PAC concentration of only 5 mg/L. Contact time does not factor into the ability of Acticarb to reduce DOC. As was the case with the Red Lake River water, the Cal-Pacific PAC DOC removal data could not be reduced to a valid model that met the 85% confidence interval criterion.

3.4.2 Activated Carbons

3.4.2.1 Acticarb

Maximum reductions in DOC predicted by the Acticarb models ranged from 20% to 39%. It appears that Acticarb's sorption capabilities are overridden by water parameters. The plots in Appendix A show that the "best" conditions for this PAC are different for different situations.

3.4.2.2 Cal-Pacific

Cal-Pacific PAC did not prove to be very effective at reducing DOC. The Cal-Pacific PAC did reduce DOC from Park River water at all conditions, but by a predicted maximum of only about 33%, and for Mississippi River water by a predicted 5% only at high temperatures and high PAC concentrations. The actual DOC reduction data points were so scattered that a model meeting the 85% confidence level could not be made for the Cal-Pacific PAC with either Missouri River or Red Lake River waters.

3.4.2.3 Knife River

The models predicted that Knife River PAC would reduce DOC levels by as much as 21%, 34%, and 48% for Mississippi River, Missouri River, and Park River waters, respectively. The model predicted that Knife River carbon would not reduce the DOC levels for Red Lake River water. The statistical analysis indicates that Knife River PAC tends to interact fairly simply when sorbing DOC. This is seen in the few number of terms found in the models. However, the plots in Appendix B show that a specific set of conditions at which the PAC performs the best for all waters does not exist.

3.4.2.4 Freedom

Freedom PAC reduced DOC levels by amounts ranging from 21% to 39%, although there were some conditions at which it is not predicted to reduce DOC for water from the Mississippi River (i.e., at PAC concentrations less than 30 mg/L). In general, the regression analysis showed that the interaction between Freedom PAC and the various waters was complex: all of the models included PAC concentration and temperature as important variables and all but one (Mississippi River water) also included time effects. One commonality between the models is the fact that Freedom PAC always seems to reduce DOC the most when the PAC concentration is the highest.

3.4.2.5 Darco Norit

Darco Norit reduced DOC levels in all of the waters tested. It was not as effective with Red Lake River water, predicted to reduce DOC by less than 20% at the highest PAC loading. However, for the other three waters, it produced the best DOC reductions and was even predicted to drop DOC levels by more than 50% for both Missouri River and Park River waters. The models describing the DOC reductions by Darco Norit are fairly complex, including PAC concentration, time, and temperature terms for three of the waters. The model describing the relationship between Darco

Norit and Red Lake River water is simpler, with PAC concentration being the only important variable. Darco Norit is predicted to reduce DOC levels best when the PAC concentration is the highest.

Some general observations that can be drawn from the results of the regression analysis include the following:

- Darco Norit PAC is the most effective of the sorbents tested. The second most effective sorbent is Acticarb, followed in descending order of average predicted DOC reduction by Freedom, Knife River, and Cal-Pacific PAC.
- Cal-Pacific PAC is not an effective DOC sorbent.
- The greatest DOC reduction for each of the waters was achieved when the concentration of the most effective sorbent was 100 mg/L.
- Park River water DOC is reduced the best at the lowest temperatures and the shortest contact times.

3.5 Practical and Economic Considerations

A key consideration is the ability of the selected PACs to achieve DOC reductions that will allow the treated water to comply with DBP regulations. In order to evaluate the conditions tested, a relationship between THMfp and DOC was developed for each water–PAC combination. This relationship was used to evaluate the ability of PAC to achieve an 80-ppb THMfp level in the treated waters within the limits of the test conditions. Under the conditions tested, none of the PACs was capable of achieving a treated-water target of less than 80 ppb THMfp when treating Mississippi River water – a source water with a high THMfp. Source water with a relatively low THMfp, such as from the Missouri River, was effectively treated using PAC under a variety of test conditions. Table 8 lists the conditions where the respective PACs were predicted to reduce THMfp to less than 80 ppb in the treated waters.

For each successful water–PAC combination, preliminary cost scenarios were developed. Retail costs of the PAC products were assumed to be the same for all products and estimated to be \$650/ton. Shipping costs were estimated to be \$2.60/20 ton-mile. It was assumed that the Acticarb and Darco products would be produced and shipped from Tampa, Florida, and Dallas, Texas, respectively. For purposes of comparison, it was assumed that an activated carbon production plant producing PAC from lignite out of either the Freedom or Knife River mines would be sited in central North Dakota. For a 15-MGD water treatment plant located in eastern North Dakota, a \$50/day cost savings (23%) could be realized when treating water with the character of the Missouri River. A higher savings could be realized when treating water with a higher THMfp, such as the Red Lake River. While utilities are typically bound to a low carbon price that meets the necessary specification, the overall economics will depend on water type and the ability of the activated carbons to achieve

TABLE 8

Predicted PAC Dose and Temperature Range for Desired Treatment

Source Water	PAC	Temperature Range	Required Dose
Missouri River	Acticarb	23° to 25°C	5 mg/L
	Knife River	25°C	5 mg/L
	Freedom	14° to 25°C	5 mg/L
	Darco Norit	17° to 25°C	5 to 100 mg/L
Red Lake River	Acticarb	5° to 15.9°C	22 to 100 mg/L
	Freedom	5° to 25°C	17 to 73 mg/L
	Darco Norit	5° to 25°C	42 mg/L
Park River	Acticarb	24.25°C	100 mg/L
	Knife River	5° to 19°C	5 to 95 mg/L
	Freedom	5° to 25°C	44 to 61 mg/L
	Darco Norit	5° to 25°C	54 to 59 mg/L

a desired reduction. The greatest variable is the distance that a selected PAC product would have to be transported. Thus a production facility in North Dakota would have an economic advantage for midwestern water utilities. A more detailed market analysis, well beyond the scope of this research, would be needed to establish the economic viability of an activated carbon production facility.

4.0 CONCLUSIONS

This project has shown that activated carbons produced from North Dakota lignites are, in many cases, effective at reducing NOM from water to levels that will satisfy promulgated levels of DBPs in finished public water supplies. Comparisons of North Dakota lignite-derived activated carbons to commercially available products have indicated comparable performance. This performance, however, is dependent on the quality of the raw water supply. The best treatment performance is realized with relatively low levels of DOC and, subsequently, lower THM formation potential. High levels of NOM limited the effectiveness of the activated carbons to achieve a necessary organics removal in order to satisfy regulatory standards.

Activated carbons produced from North Dakota lignite yield PAC with a relatively low surface area because of the effects of carbon burnout in the presence of sodium. Product yields under the carbonization and steam activation conditions used during this study were approximately 35%. Activated carbon production methods for this study made use of a small tube furnace to produce several batches of material, and there was a certain degree of variability of product with each batch. Process control is an important consideration in the production of activated carbons and requires continuous monitoring and adjustment of process control parameters to produce a product carbon with uniform consistency. Additional investigation using continuous feed processing is warranted in order to demonstrate and scale up design process production parameters.

Owing to the high reactivity of the sodium during activation, more aggressive activation conditions to produce carbons with higher surface area result in ashing of the lignite. The reactive lignite char structures are very sensitive to the effects of the sodium in promoting gas production, even at the relatively low temperatures used in the activation. Thus longer activation times give high ash carbons and low yields. This reactivity may also be a major factor in the variability in batch productions in the bench-scale activation experiments. High sodium content is certainly one of the factors determining reactivity in the combustion and gasification of lignite.

Removal of the sodium from the lignite by ion exchange may alleviate excessive gasification encountered in the activation. The lignite char is likely to be fairly reactive even after exchange of the sodium, so that a microporous carbon could be produced at longer activation times. With less burnout of carbon, more micropores would be left. It is also likely that the micropore dimensions would also increase as a result of the additional activation time. Both of these effects would thus lead to much higher surface areas in the demineralized carbons.

This work examined the effects of activated carbon addition only, without regard for any synergistic effects of other treatment, such as coagulation or softening. In most water treatment plants, activated carbon would be used in presedimentation basins along with other treatment chemicals such as alum and polymers to precipitate suspended and colloidal solids and remove organic constituents. The combined effects of carbon sorption and optimized downstream treatment operations can be anticipated to impact the removal of organic matter and reduce the dose of PAC or other chemicals. This may also improve the effectiveness of organics removal in waters with high THM formation potential that did not show effective treatment using activated carbon alone.

The study described herein evaluated DOC removals sufficient to satisfy THM formation potential at $\leq$80 ppb. The THM formation potential test provides an indication of the maximum amount of THM that will be produced from a given water sample without the typical constraints of disinfectant concentration or contact time. In actual water treatment processes, there are practical and regulatory limits to disinfectant concentration and contact time. Therefore, the results discussed above provide a “worst-case” scenario with respect to “acceptable” DOC removal by the various PACs under the conditions evaluated.

Future work should address other applications and potential markets for North Dakota lignite-derive PACs, including applications for agricultural processing and industrial wastewater treatment uses, as well as the potential for contaminated site cleanup and remediation.

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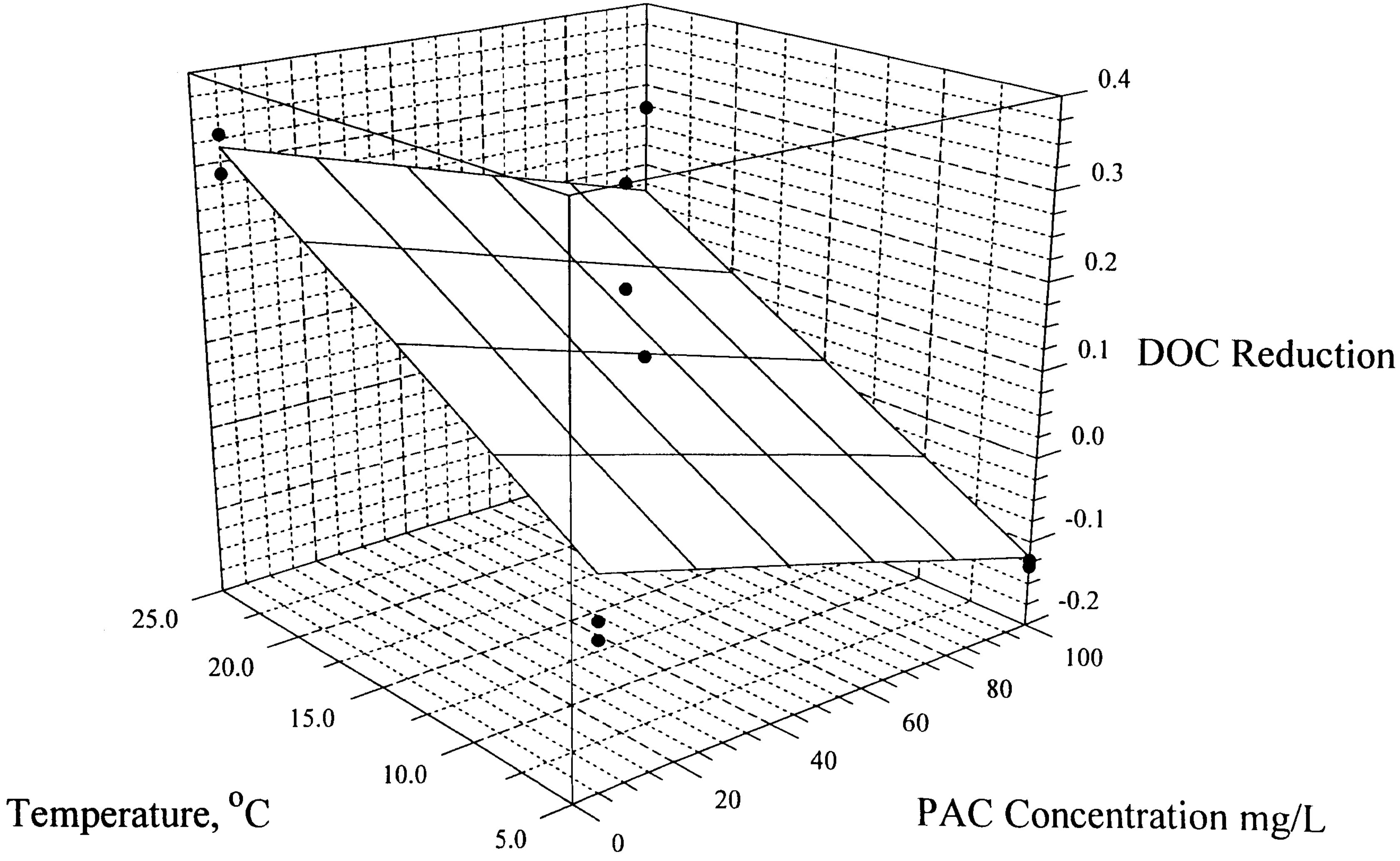
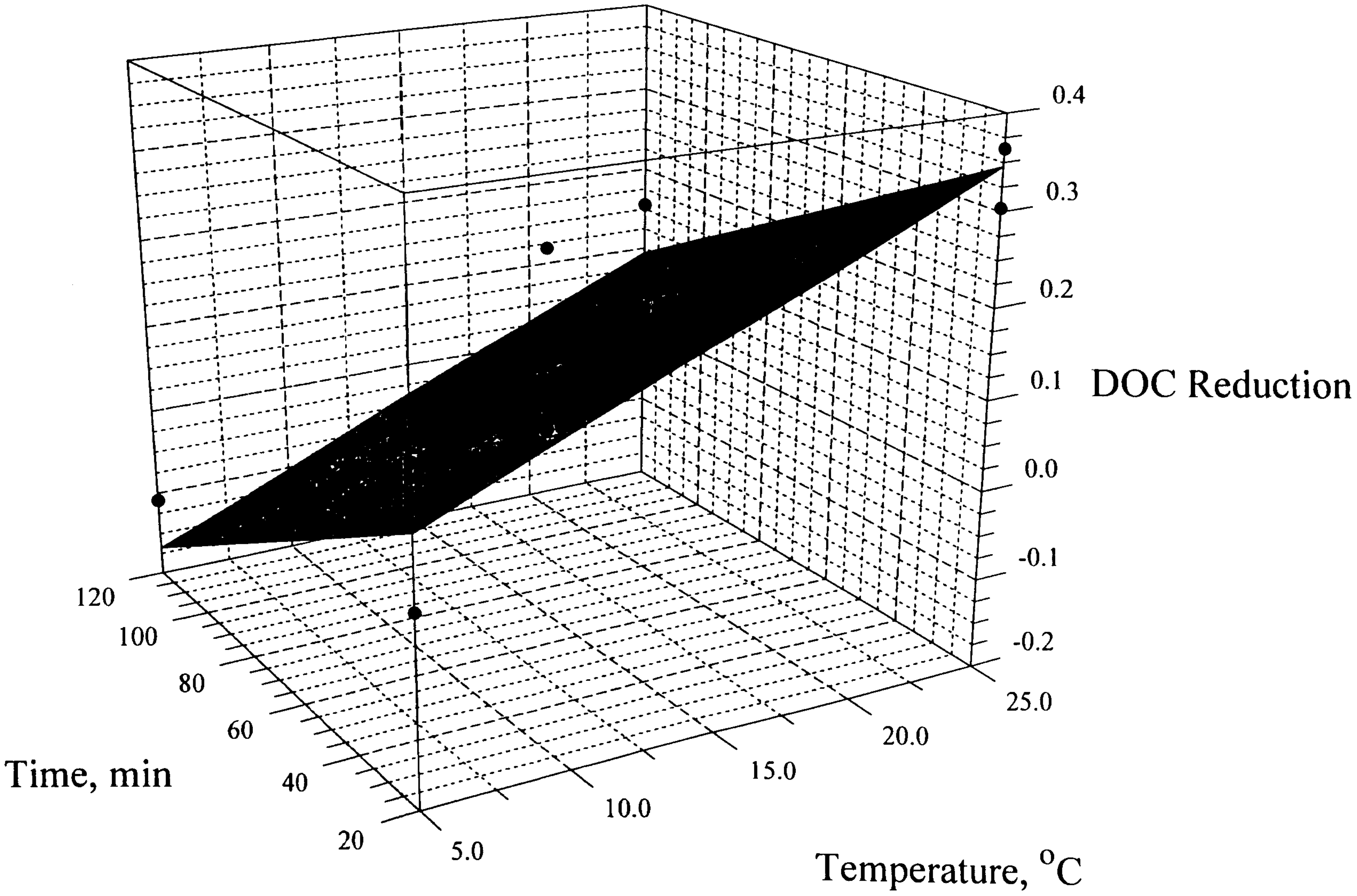
APPENDIX A

DOSE–RESPONSE RELATIONSHIP PLOTS

Acticarb PAC/Missouri River Water

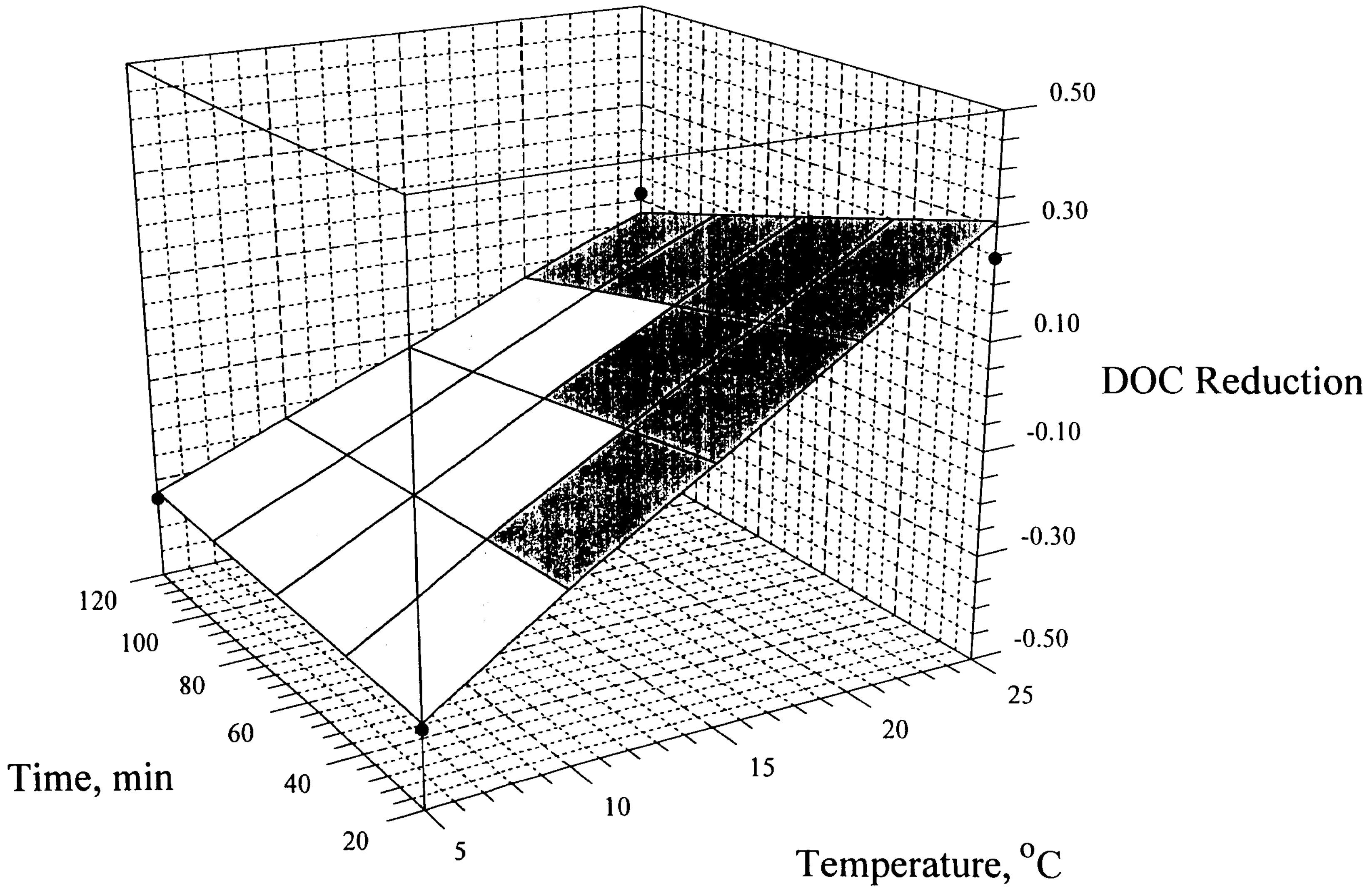


Knife River PAC/Missouri River Water



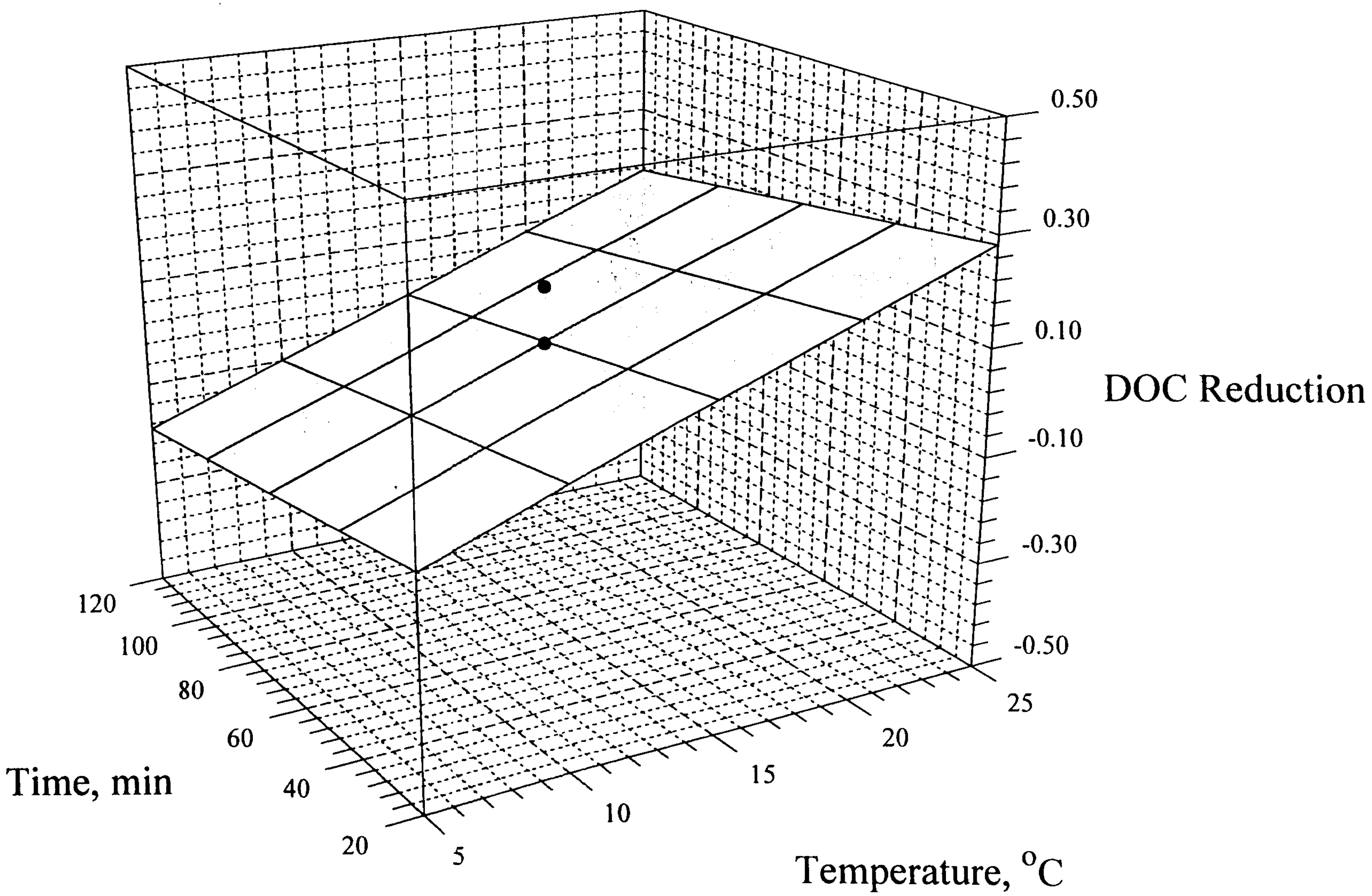
Freedom PAC/Missouri River Water

PAC Concentration = 100 mg/L



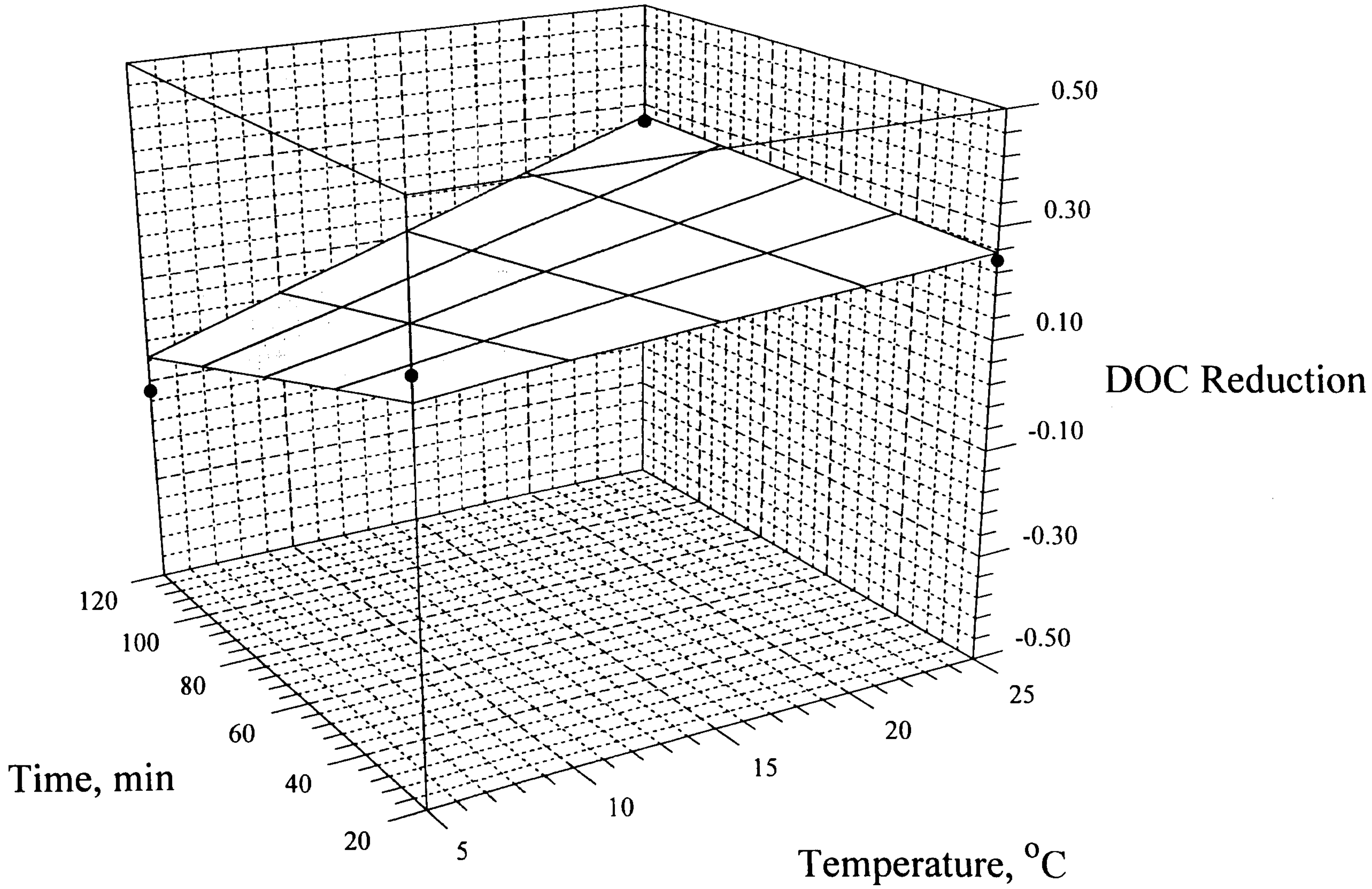
Freedom PAC/Missouri River Water

PAC Concentration = 52.5 mg/L

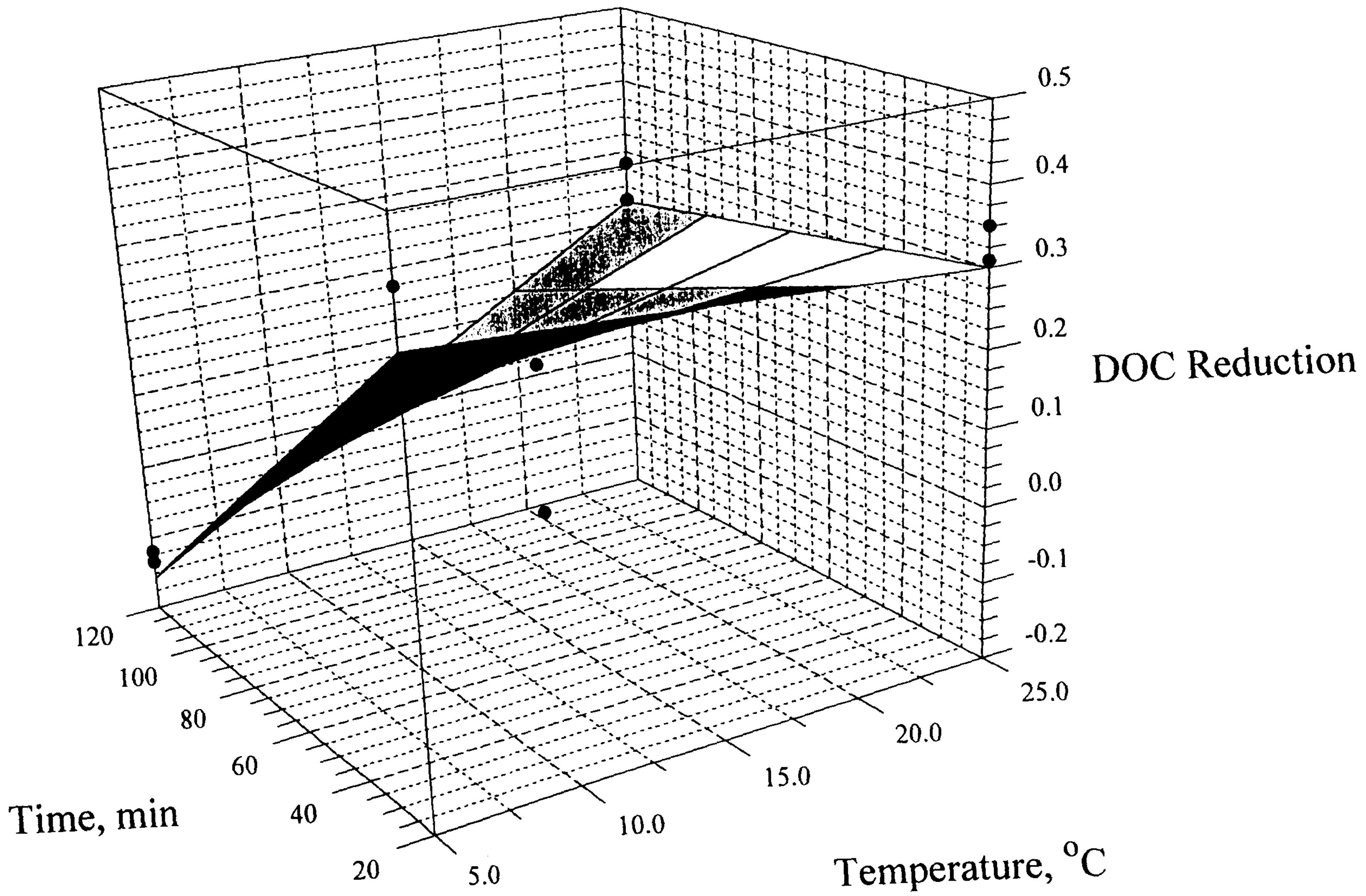


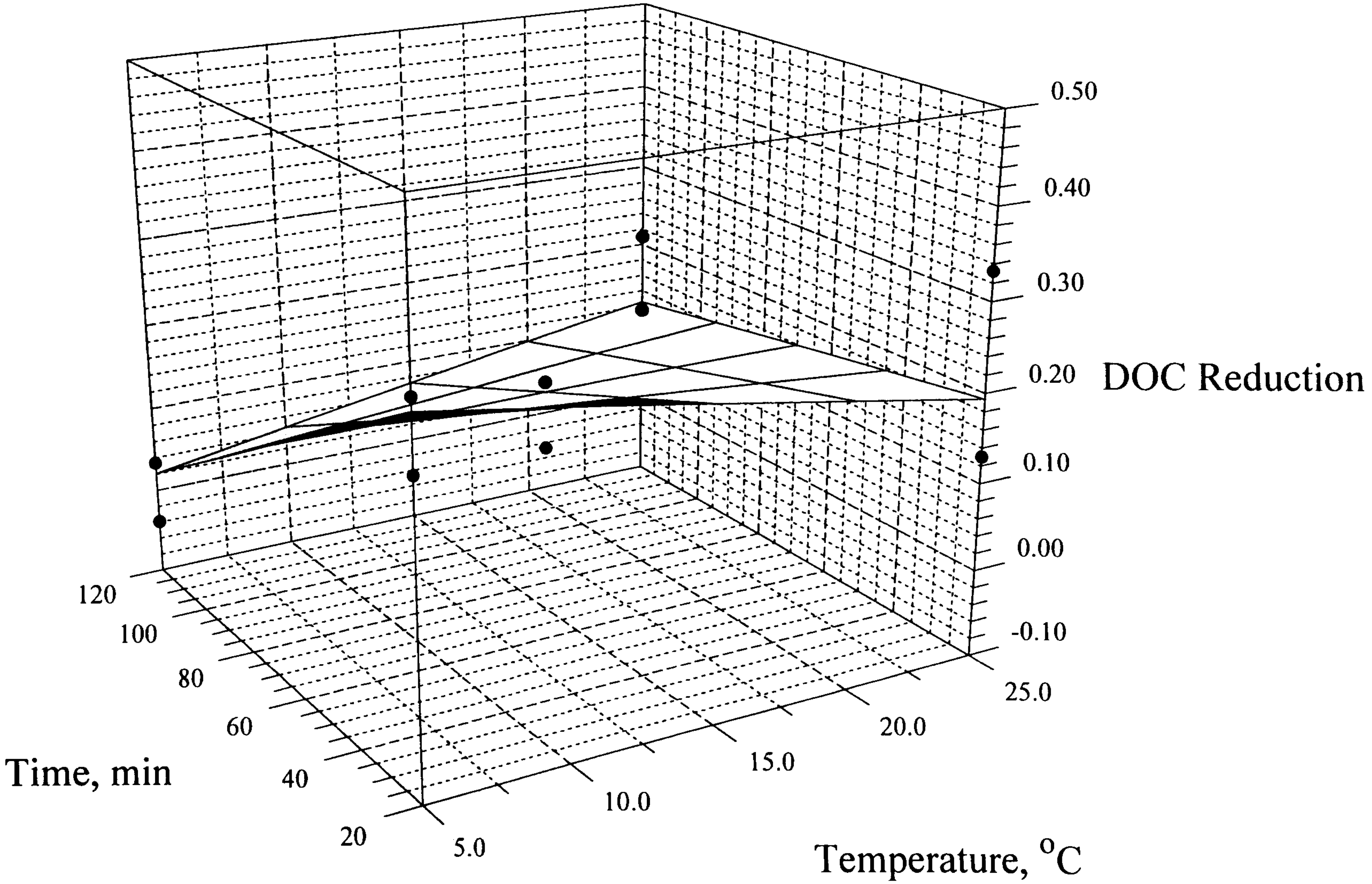
Freedom PAC/Missouri River Water

PAC Concentration = 5 mg/L



Acticarb PAC/Park River Water

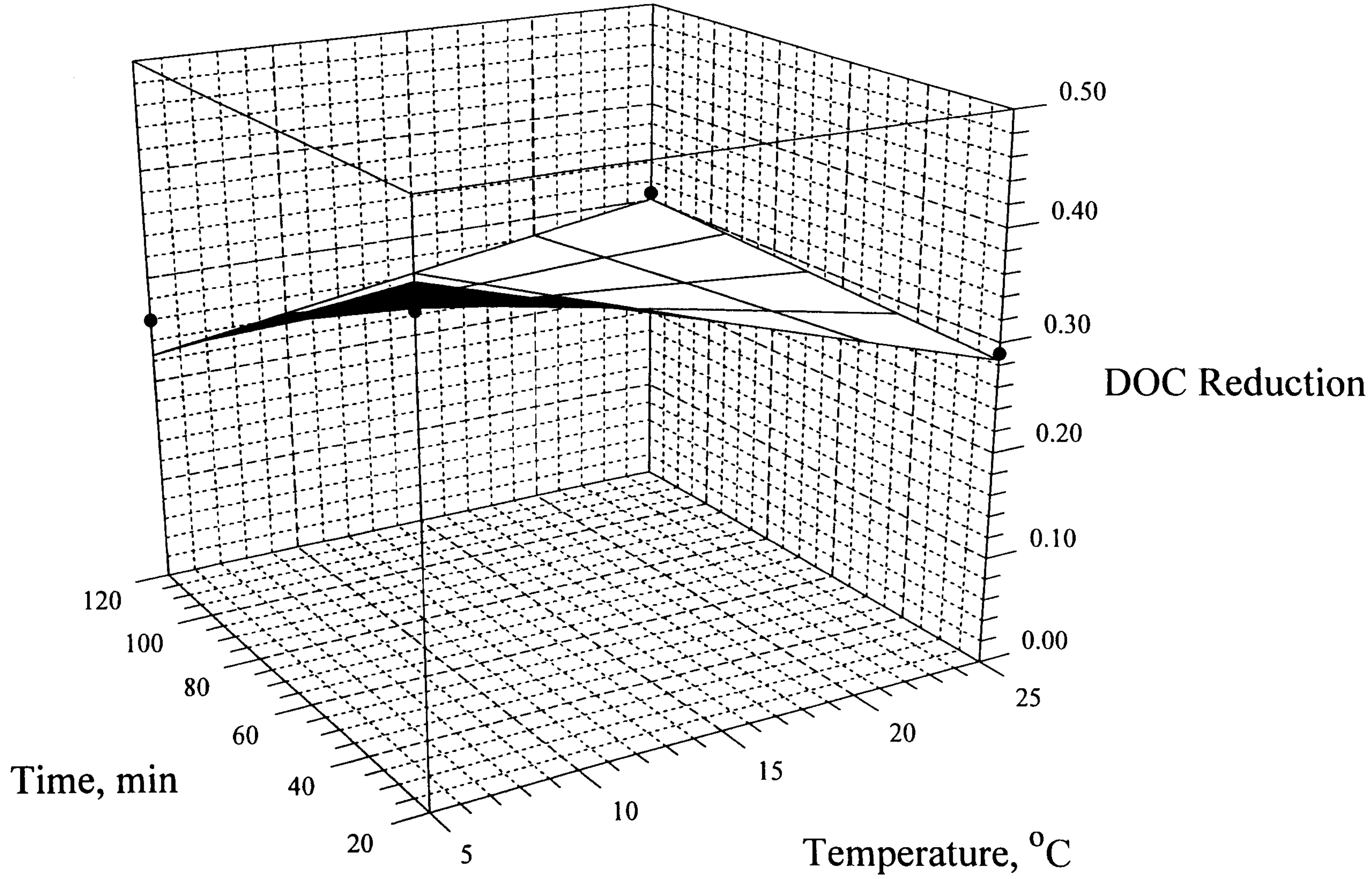




Cal-Pacific PAC/Park River Water

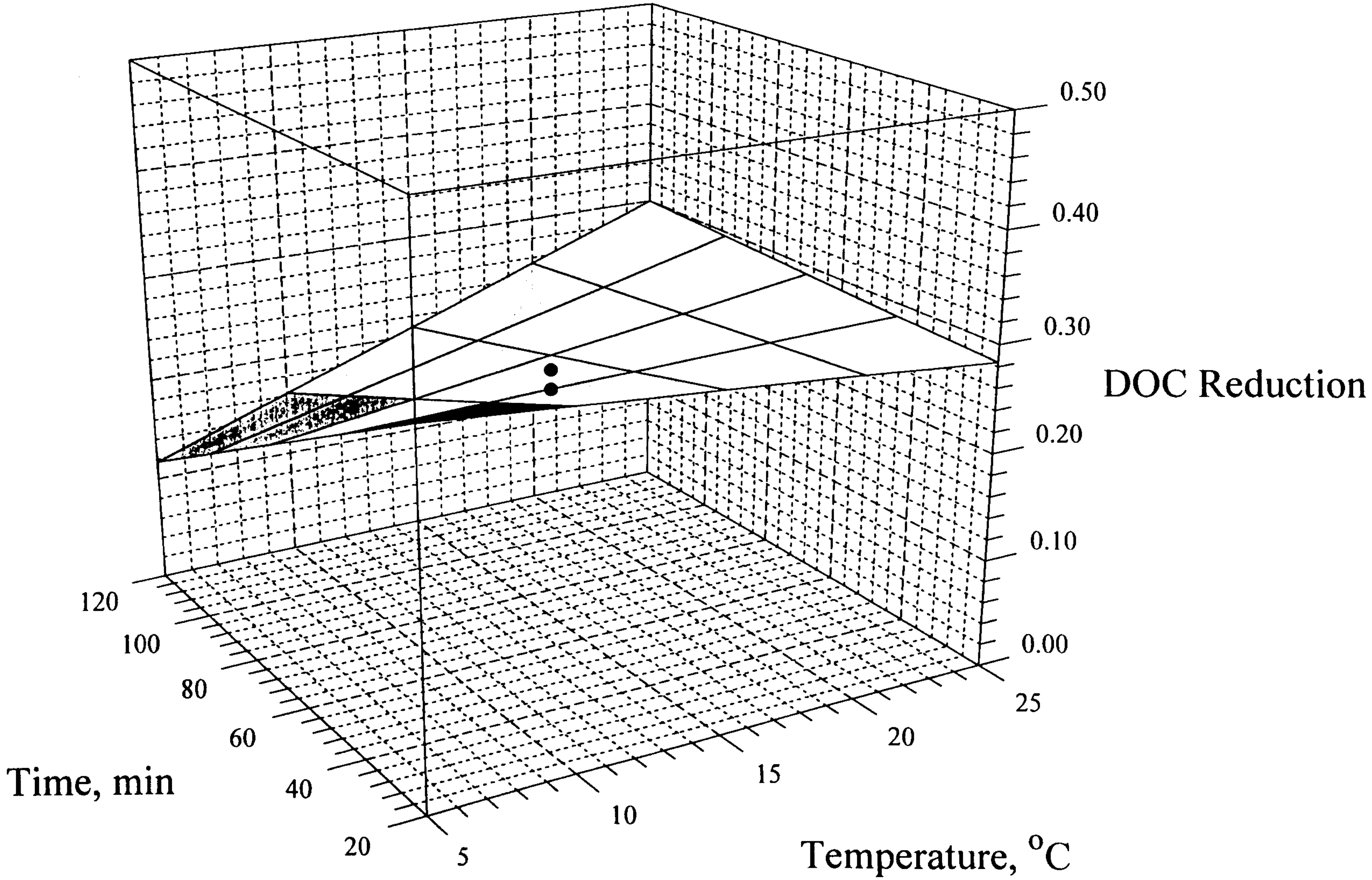
Knife River PAC/Park River Water

PAC Concentration = 100 mg/L



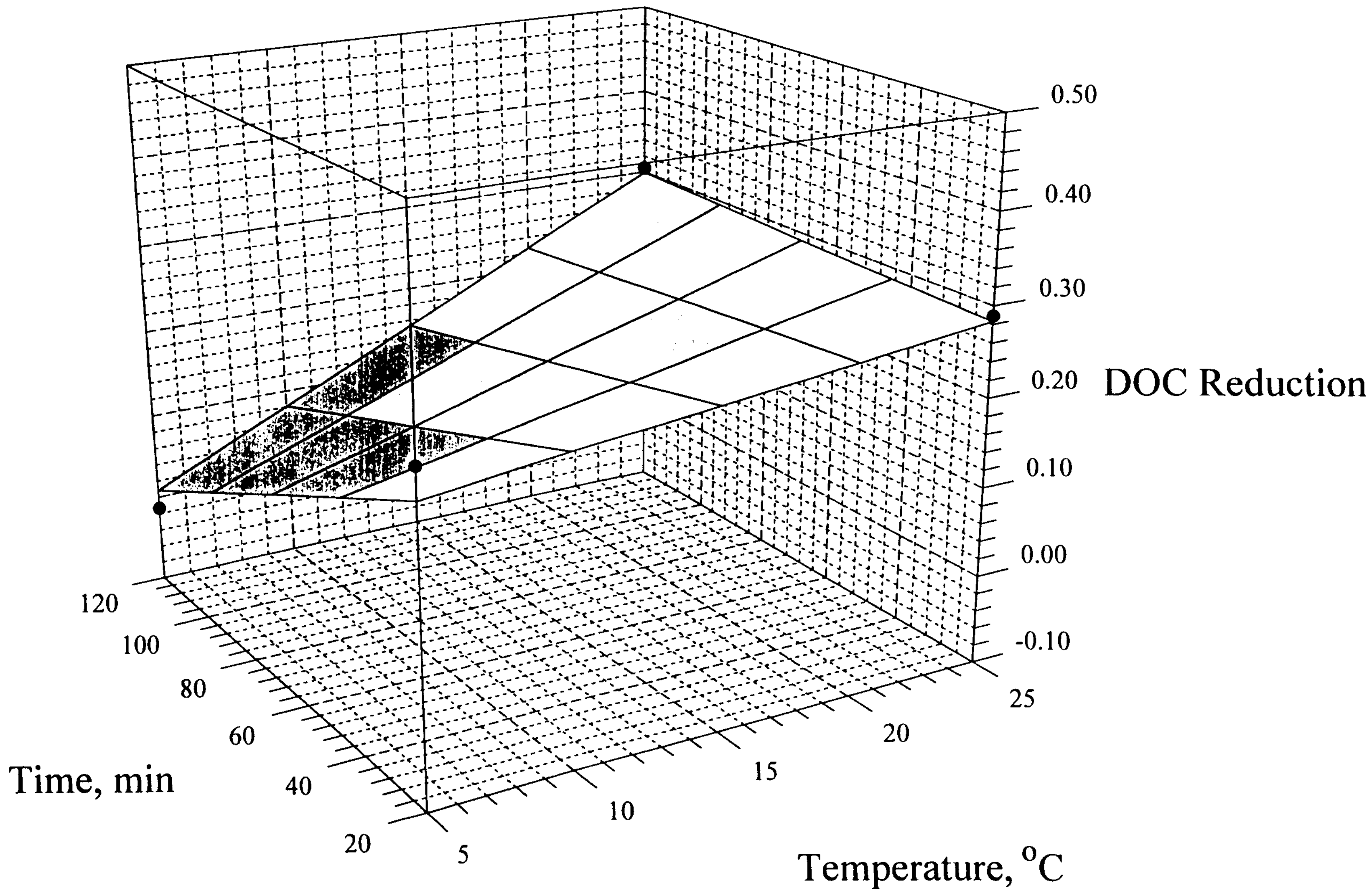
Knife River PAC/Park River Water

PAC Concentration = 52.5 mg/L



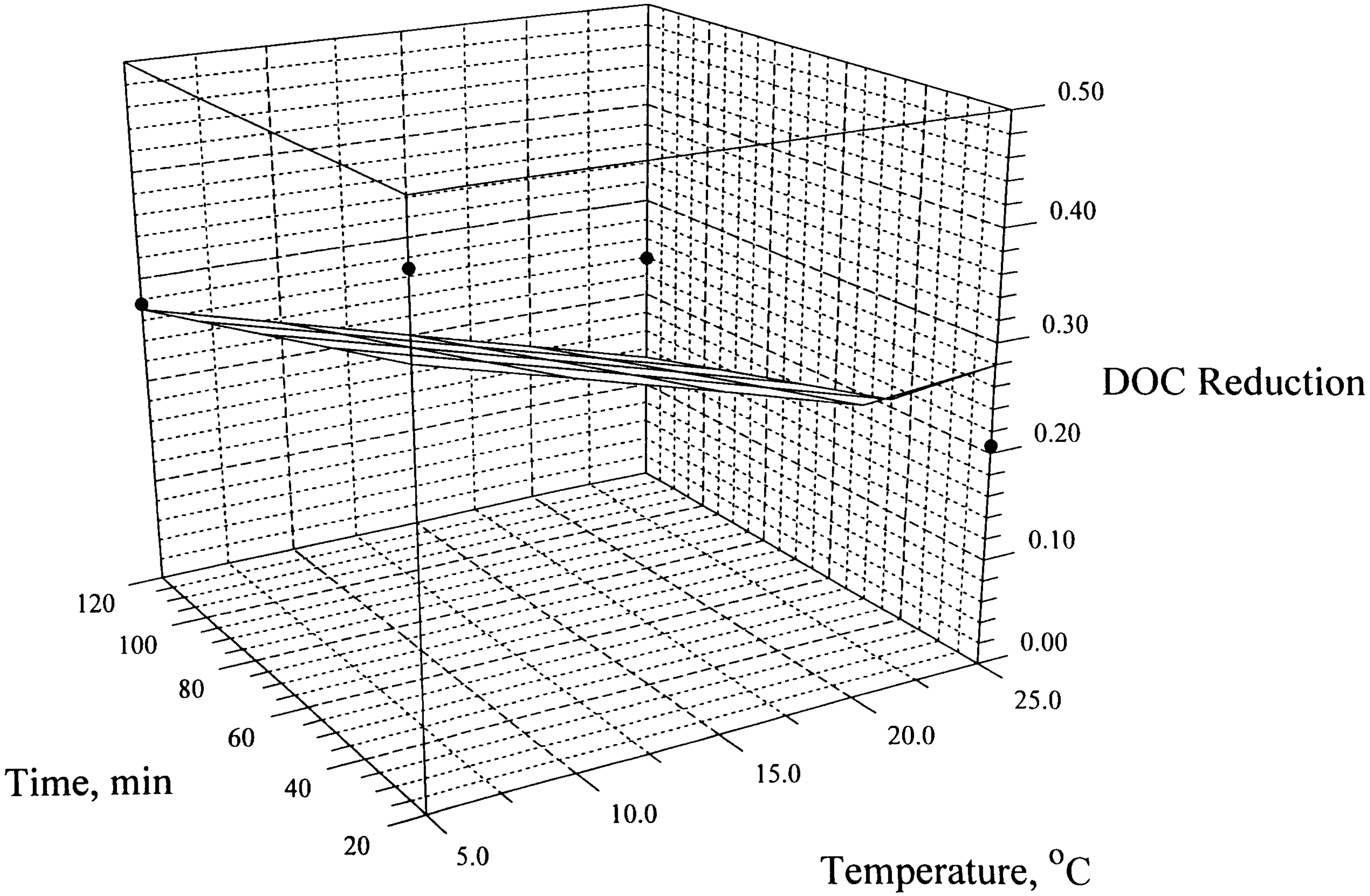
Knife River PAC/Park River Water

PAC Concentration = 5 mg/L



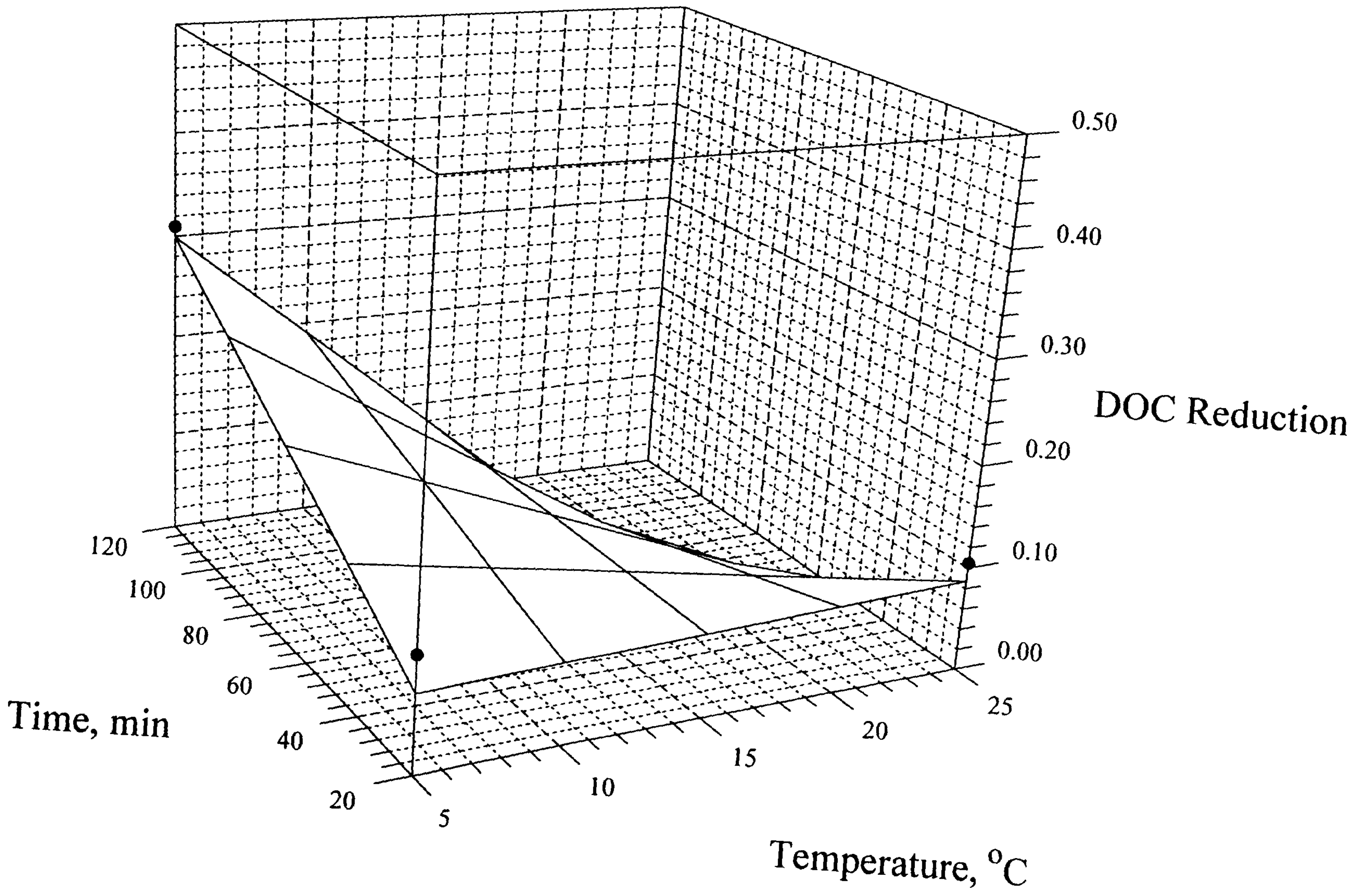
Freedom PAC/Park River Water

PAC Concentration = 100 mg/L



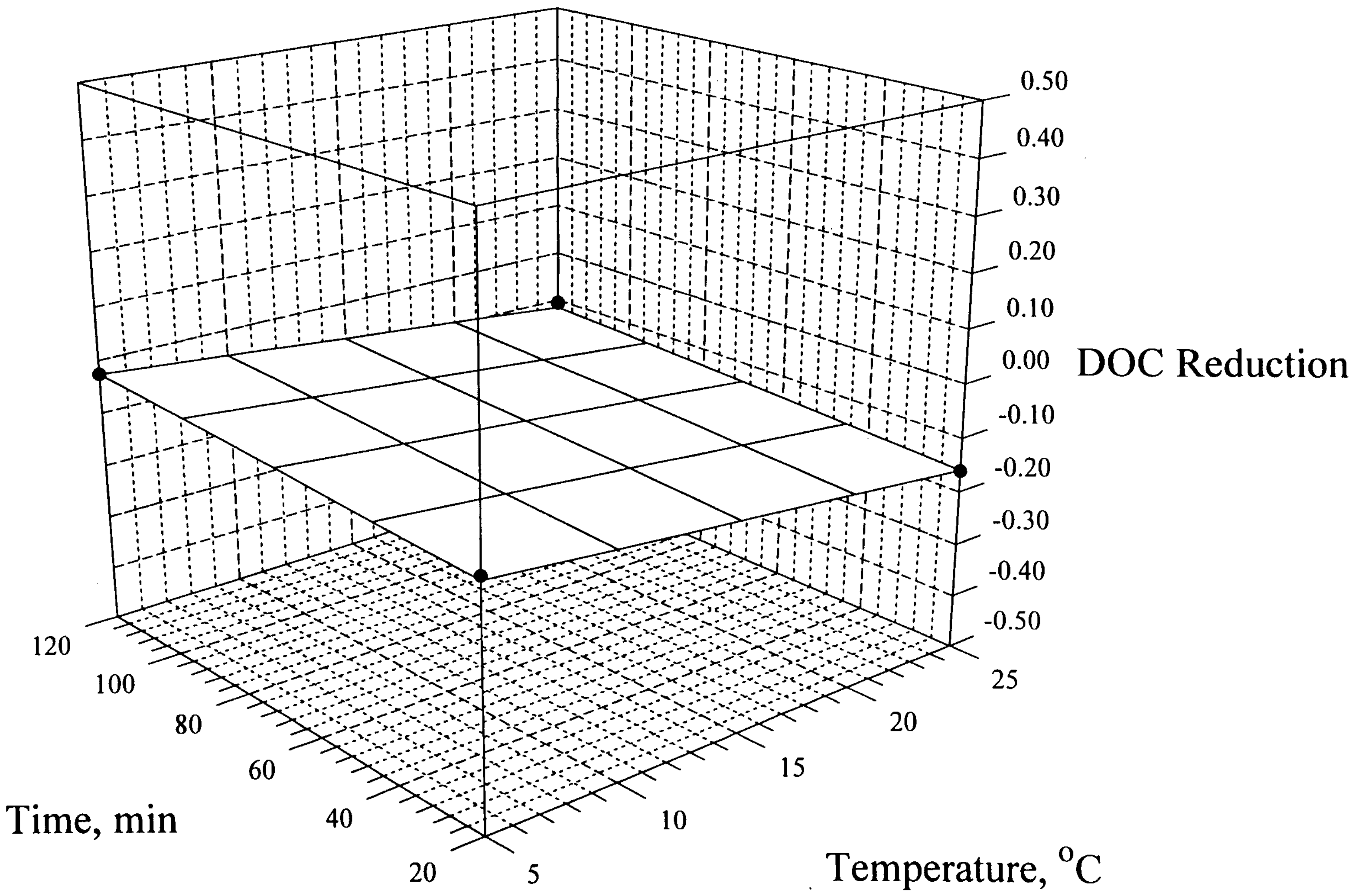
Acticarb PAC/Red Lake River Water

PAC Concentration = 100 mg/L

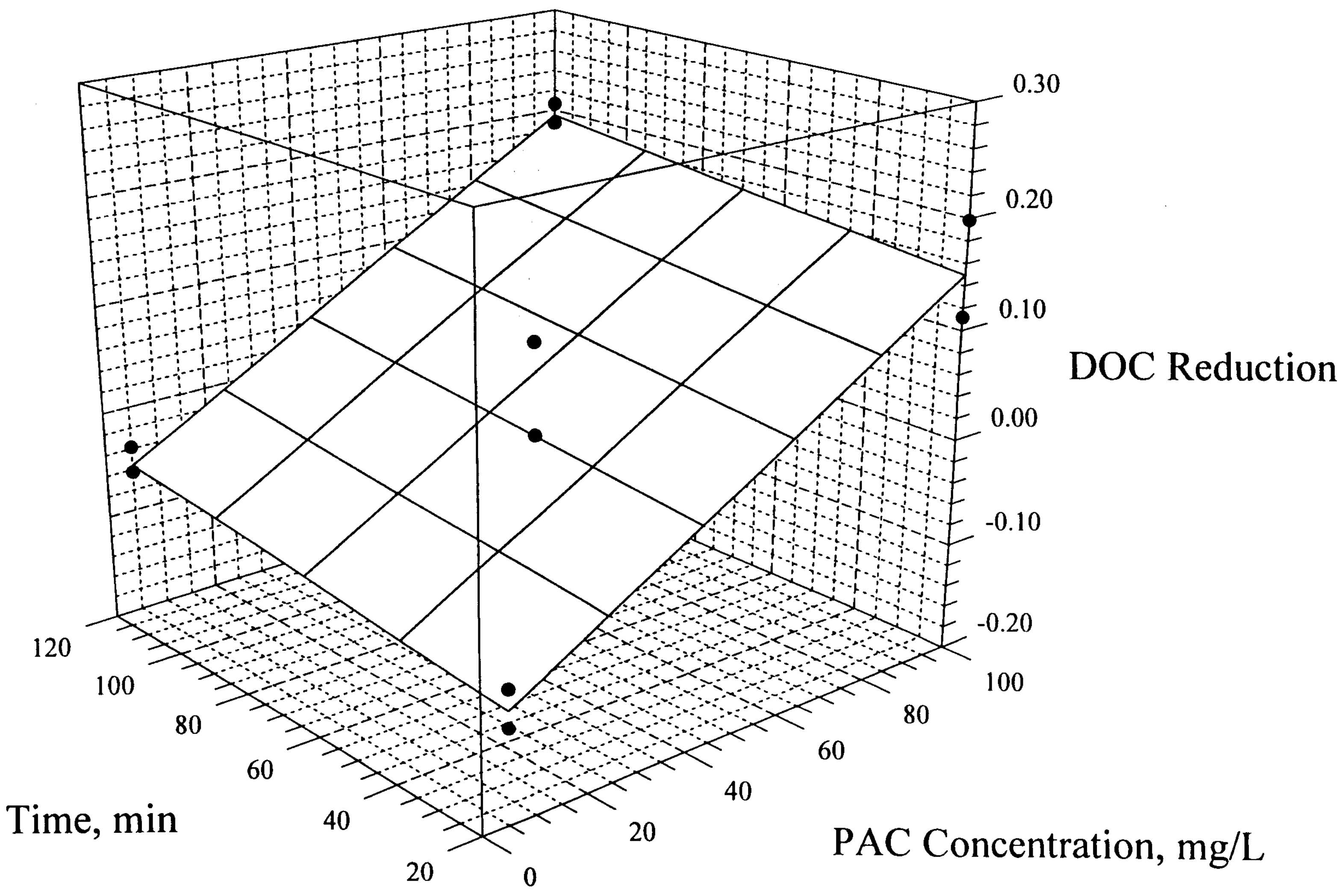


Darco Norit PAC/Mississippi River Water

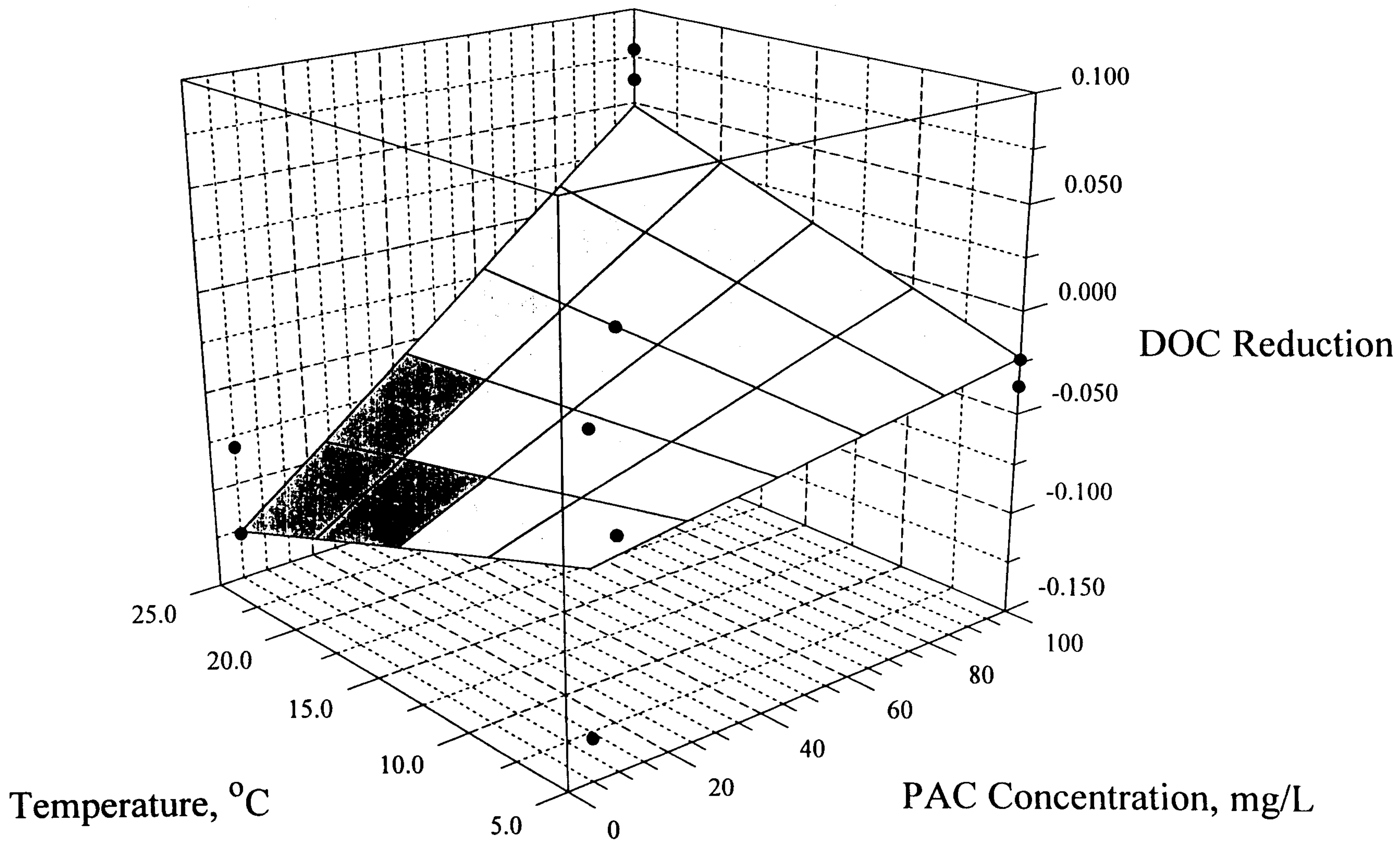
PAC Concentration = 5 mg/L



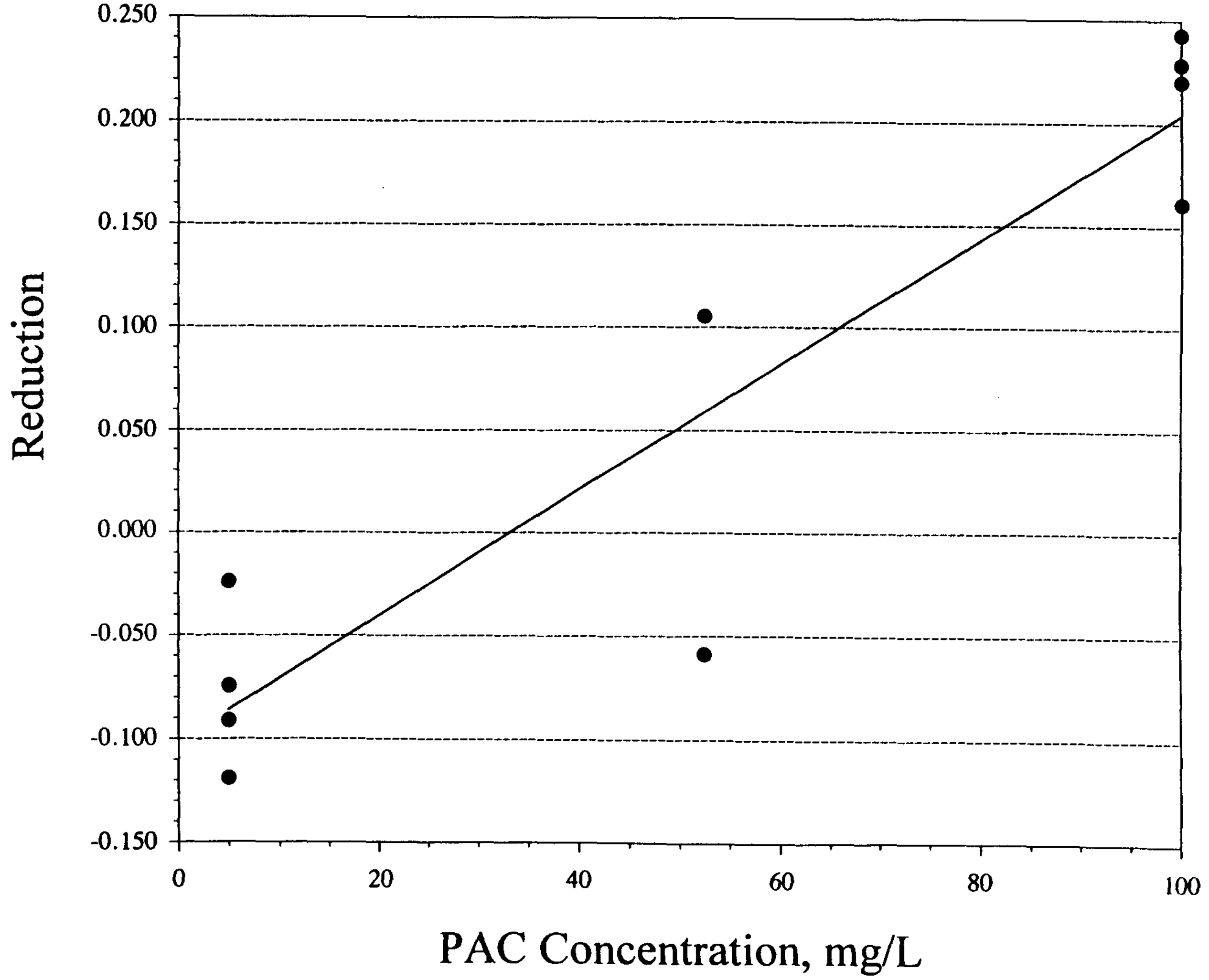
Acticarb PAC/Mississippi River Water



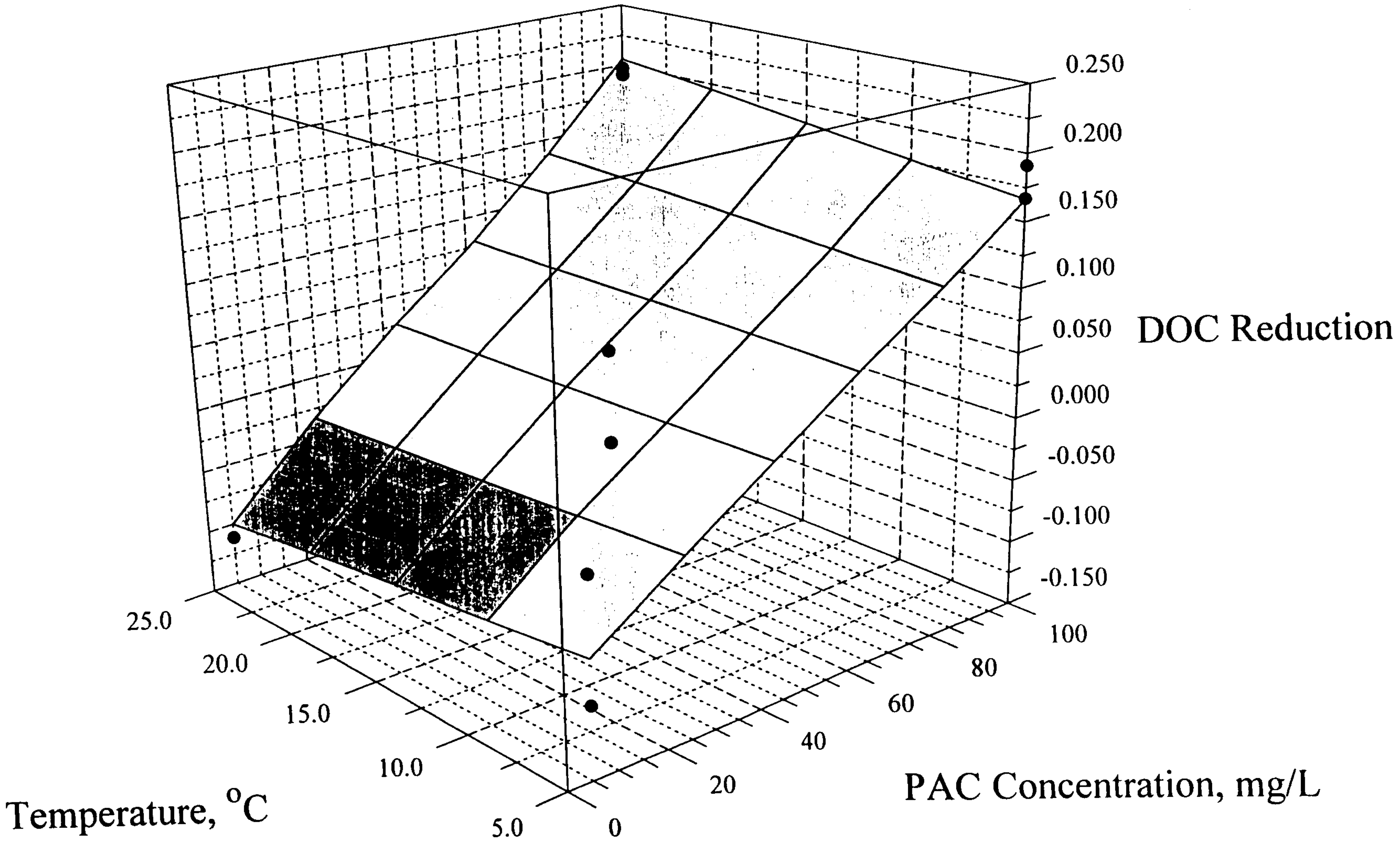
Cal-Pacific PAC/Mississippi River Water



Knife River PAC/Mississippi River Water



Freedom PAC/Mississippi River Water



Darco Norit PAC/Mississippi River Water

PAC Concentration = 100 mg/L