MODELING THE COMPETITIVE ADSORPTION OF 1,1,2-TRICHLOROETHANE WITH NATURALLY OCCURRING BACKGROUND ORGANICS ONTO ACTIVATED CARBON

by

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A Thesis
Submitted to the School of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University

 1985

COMPETITIVE ADSORPTION MODELING

DOCTOR OF PHILOSOPHY (1985) McMASTER UNIVERSITY
(Chemical Engineering) Hamilton, Ontario

TITLE: Modeling the Competitive Adsorption of 1,1,2-Trichloroethane with Naturally Occurring Background Organics onto Activated Carbon

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NUMBER OF PAGES: xix, 244

ABSTRACT

Activated carbon adsorption is the most widely considered process for the removal from drinking water of low level toxic chemicals as well as many other organic substances. The adsorption of these compounds involves complex competitive interactions which are not well understood, however, they are crucial to the design of safe and cost effective adsorbers. To obtain a better understanding of competitive adsorption as observed in water treatment adsorbers at the time of a toxic spill, a three part study was conducted with a representative bisolute mixture. The mixture consisted of a toxic chemical (1,1,2-trichloroethane (TCEA)) and the naturally occurring organic substances from a northern river considered as a single compound and measured as Total Organic Carbon.

The first part of this study consisted of single solute adsorption and desorption experiments as well as bisolute equilibrium experiments. The adsorption of TCEA was found to be completely reversible, while that of the background organics was virtually irreversible. The bisolute experiments showed that the background organics substantially decreased the adsorption capacity of TCEA, while the adsorption capacity of the background organics was only marginally reduced by the presence of TCEA. The predictive multisolute isotherm models in the literature could not describe the experimental data. Two other models, which assume that a fraction of the adsorption does not involve competition, were found to describe the data successfully.

The second part of this study investigated the rates of adsorption from one-adsorbate and two-adsorbate solutions. The data of

both single adsorbate kinetic experiments were described very well by the homogeneous surface diffusion model. The adsorption of the background organics was very slow, yet it was not necessary to utilize separate terms for the slow and rapid adsorption mechanisms. All of the adsorption occurred by the slow mechanism. The slow adsorption phenomenon, which is suspected to occur in very small pores, appears to be related to the irreversible adsorption observed during equilibrium studies. The background organics that adsorbed by the slow mechanism were virtually not desorbable, while TCEA which adsorbed completely reversibly, did not show any slow adsorption during the kinetics. As expected from the large difference in the values of the diffusion coefficients, to properly model the bisolute batch kinetic experimental data, diffusional interactions such as cross diffusion terms had to be included.

The third part of this investigation was a column study involving six different phases, each with a different feed solution. The results were consistent with the equilibrium predictions. Phase IV showed that an expected and potentially dangerous large scale desorption of previously adsorbed toxic organics, caused by a substantial increase in the feed background organics, did not occur. The elution of TCEA actually decreased, probably due to cross diffusional interactions. The column experiment also confirmed that due to competitive interactions and to the increasing loading of background organics on the carbon with time, the adsorbers became substantially less effective at treating toxic spills as the operation cycle proceeded.

ACKNOWLEDGEMENTS

The author wishes to express his appreciation to all those who contributed to this work. He is particularly indebted:

to his supervisor, Dr. A. Benedek, for his guidance, encouragement and financial assistance;

to the members of the supervisory committee, Dr. C.M. Crowe, Dr. M.A. Quilliam and Dr. M. Tsezos, for their helpful suggestions;

to Zenon Environmental Inc., for financial support of the experimental program and for use of the analytical equipment;

to the Department of Chemical Engineering, for their financial support and for the use of their facilities;

to the graduate students of the Water Research group, and in particular, J.L. Bersillon, E. Diamadopoulos and J. Bell, for their many helpful discussions;

to M. Pedgic, M. Smith and J.J. Bancsi, for their cooperation;

to the staff of the Department of Chemical Engineering, particularly R.S. Hood and L. Sugget, for their cooperation;

finally and most of all, to his wife Lucy, for typing the manuscript and for the constant encouragement, help and sacrifice which permitted him to complete this study.

TABLE OF CONTENTS

NOMENCLATURE

Symbol		Equation
Å	Angstrom	
A	Surface area of the adsorbent	(2.14)
a_i	Parameter of the Radke and Prausnitz single solute models	(2.21)
a_{ij}	Coefficient of the Fritz and Schlunder competitive isotherm model	(2.20)
b	Energy constant in Langmuir isotherm model, cm^3/g	(2.5)
b_i	Energy constant for component i for the Langmuir based predictive models	
b_j	Energy constant for component j for the Langmuir based predictive models	
b_{ij}	Coefficient of the Fritz and Schlunder competitive isotherm model	(2.20)
c	Equilibrium liquid phase solute concentration, g/cm^3	
c'	Liquid phase solute concentration, g/cm^3	
c_o	Initial liquid phase concentration for the isotherms	
c_o'	Initial liquid phase concentration for the batch kinetics	(5.10)
c_{od}	Initial liquid phase concentration for the desorption cycle, mg/ℓ	(E1.8)
c_{des}	Equilibrium liquid phase concentration after the desorption cycle, g/cm^3	(4.4)
c_i	liquid phase concentration of adsorbate i, mole/l	(2.7)
c_i^o	liquid phase concentration of solute i when that solute adsorbs alone at the same temperature and spreading pressure as those of the mixture, mole/l	(2.14) (2.15) (2.16)
c_s'	Liquid phase concentration at the surface of the particles, g/cm^3	(5.1)
C	Reduced liquid phase solute concentration	(5.10)
C_s	Reduced liquid phase solute concentration at the surface of the particles	(5.15)
d_i	Coefficient of the Fritz and Schlunder competitive isotherm model	(2.20)
D	Determinant of the variance covariance matrix	

	of the residuals	
D_l	Free liquid diffusivity, cm^2/sec	(2.24)
D_s	Apparent surface diffusion coefficient, cm^2/sec	(2.23)
	In dual rate models: Surface diffusion coefficient in the macropores	(5.2)
$D_{s_{ij}}$	Cross diffusion coefficient of solute i caused by solute j, cm^2/sec	(5.28)
D_p	Apparent pore diffusion coefficient, cm^2/sec	(2.22)
f	Fraction of the total particle capacity in the macropores	(5.2)
g_1	Constant in equations 4.5 and 4.6	(4.5) (4.6)
g_2	Constant in equations 4.5 and 4.6	(4.5) (4.6)
g_3	Constant in equation 4.6	(4.6)
g_4	Constant in equation 4.6	(4.6)
k	Constant in Freundlich isotherm model	(2.6)
k_b	Pseudo mass transfer coefficient for transport to the branch pores, 1/sec	(5.3)
k_f	External mass transfer coefficient, cm/sec	(5.1)
k_i	Constant for component i for Freundlich based competitive isotherm models	
L	Constant in isotherm model	(2.1) (2.2)
M	Mass of carbon used in the adsorption cycle, g	(E1.1)
M_{des}	Mass of carbon used in the desorption cycle, g	(E1.8)
n	Constant in Freundlich isotherm model	(2.6)
n_i	Constant for component i for Freundlich based competitive isotherm models	
NC	Number of adsorbates in competition	
p_i	Non-ideal adsorption correction term for solute i in ISIAS model	
q	Equilibrium solid phase concentration, g/g	
q'	Solid phase concentration, g/g	

q_b'	Solid phase concentration in the branch pores, g/g	(5.3)
q_{des}	Equilibrium solid phase concentration after the desorption cycle, g/g	
q_i	Solid phase concentration of adsorbate i in all competitive adsorption models, g/g	
q_i^o	Solid phase concentration of solute i when that solute adsorbs alone at the same temperature and spreading pressure as those of the mixture, mole/l	(2.13) (2.14) (2.15)
q_m'	Solid phase concentration in the macropores, g/g	(5.2)
q_o'	Solid phase concentration in equilibrium with c_o'	(5.11)
q_T	Total molar concentration on the activated carbon, moles/g	(2.10) (2.11) (2.13)
q_T'	Total solid phase concentration, g/g	(5.9)
Q_b	Reduced solid phase concentration in the branch pores	(5.12)
Q_m	Reduced solid phase concentration in the macropores	(5.11)
QM	Monolayer Adsorption Capacity, g/g	
QM_i	Monolayer solid phase concentration of adsorbate i in all competitive adsorption models, g/g	
r	Particle radial variable, cm	(2.22) (2.23)
R	Universal gas constant	(2.14)
R_p	Particle radius, cm	(5.1)
R_b	Local rate of transfer, g/g/t	(5.2)
r_i	Average ratio of experimental to predicted solution concentration for species i	(2.17)
t	Time variable, sec	(2.22) (2.23)
T_a	Absolute temperature	(2.14)
V	Liquid volume in the adsorption cycle, ℓ	(E1.1)
V_{des}	Liquid volume in the desorption cycle, ℓ	(E1.8)
w_i	Fraction of overall capacity of compound i which is involved in competition	(2.18) (4.7)

z_i	Adsorbed phase mole fraction of solute i	(2.11) (2.12) (2.13) (2.16)

Greek symbols

α_i	Parameter of the Radke and Prausnitz single solute models	(2.21)
β	Reduced particle radial distance	(5.14)
β_i	Parameter of the Radke and Prausnitz single solute models	(2.21)
ε	Liquid volume fraction in the kinetic bottles	(5.1)
ε_p	Internal porosity of the particle	(2.22)
η_i	Parameter of the Radke and Prausnitz single solute models	(2.21)
π	Spreading pressure	(2.14)
σ	Standard deviation	
ρ_c	Particle density of the adsorbent, g/cm^3	(2.22) (5.4)
θ	Dimensionless time	(5.13)
ν	Tortuosity factor	(2.24)

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

COD	Chemical oxygen demand
DBS	Dodecyl benzene sulfonate
FA	Fulvic acids
FRW	Fauquier river water
GAC	Granular activated carbon
HA	Humic acids
HSSD	Homogeneous solid surface diffusion
IAS	Ideal adsorbed solution
ISIAS	Improved simplified IAS
MADAM	Michigan adsorption design and applications model
MIB	Methylisoborneol
MSCAM	Modified SCAM
ODE	Ordinary differential equation
OFW	Organic free water
PAC	Powdered activated carbon
PDE	Partial differential equation
PTS	P-toluene sulfonate
P-DBS	Phenol-DBS
P-PTS	Phenol-PTS
SCAM	Simplified competitive adsorption model
TCEA	1,1,2-trichloroethane
THM	Trihalomethanes
TOC	Total organic carbon

CHAPTER ONE

INTRODUCTION

Symons et al (1975) reported on a survey which found that water supplies throughout the United States contained a wide variety of toxic organics present in µg/ℓ levels. The sources of these organics are partially treated wastes, leaching toxic dumps, toxic spills and the byproducts of chlorination at water treatment plants. This has resulted in a variety of research projects on the quality of drinking water, by modifying treatment schemes and using additional treatment processes. Activated carbon adsorbers are the most widely considered additional treatment process because they can completely remove a very wide variety of organics. The main disadvantage of this process and its alternatives is their high cost and uncertainty with regards to removal consistency.

Thus the cost efficient design of adsorbers is of utmost importance. The design of adsorbers is complex due to the non steady state nature of the process, and therefore it is generally based on a limited number of pilot scale tests which are expensive and time consuming. Alternatively, mathematical models calibrated by relatively simple batch experiments, can be used to simulate all possible designs and operating conditions. Thus, mathematical modeling can be used to substantially reduce the cost of constructing and operating adsorbers. Narbaitz and Benedek (1983) showed in a refinery wastewater application

that a conventional design was 40 percent more expensive than the optimal design identified by mathematical modeling. Present modeling capabilities are mostly limited to the use of single water quality parameters, while most waters contain many contaminants. Thus the most common approach in modeling column adsorbers is to use lumped parameters, such as Total Organic Carbon (TOC).

A relatively short time after the column starts operating, some individual contaminants such as chloroform may start appearing in the effluent. Eventually, the effluent concentration of this compound exceeds that of the influent. The displacement of this compound from the carbon is generally called a chromatographic effect. In this case, the chromatographic effect is caused by the time dependent reequilibration process on the activated carbon which involves the competitive adsorption of the specific compound and other more strongly adsorbed organics. The occurrence of chromatographic effects which frequently would be unnoticed by the monitoring of lumped parameters, demonstrates the great need for multicomponent modeling for realistic cost efficient design methodologies.

As described in detail in the next chapter, research on multicomponent adsorption has been almost exclusively limited to millimolar concentrations of very similar compounds. However, water treatment plant adsorbers must remove a very wide variety of vastly different organics. The most prevalent are the naturally occurring background organics (humic substances), which are present in all water sources. Although these organics are harmless, Murin and Snoeyink (1979) showed that they are extremely important because they compete with the toxic organics for the adsorption sites and significantly

reduce the capacity to remove toxic organics. In addition, in water treatment plants using pre-chlorination, some of these natural organics react to form trihalomethanes, which are toxic.

The goal of this thesis is to model and predict the performance of a water treatment adsorber treating a water source contaminated by a toxic spill. This study will consider the contaminated water as a binary mixture of 1,1,2-trichloroethane, used as a model toxic compound, and the natural organics from a Northern Ontario river measured as TOC to facilitate the modeling. This represents one of the first attempts to use competitive adsorption modeling on a practical case, and it is hoped that it will lead to improved designs.

This work consists of the two basic types of experiments required for the modeling of adsorbers: equilibrium and rate studies. They will include individual solute and bisolute equilibrium experiments to determine the maximum adsorptive capacities and the competitive effects. Various competitive equilibrium models from the literature, as well as a new empirical model, will be assessed for this particular bisolute mixture. Single solute and bisolute rate tests will be used to investigate and calibrate adsorption kinetic models which include diffusional interactions. The result of this study is a general adsorption model for the prediction of water treatment adsorbers performance when treating contaminated waters.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Activated carbon has been in use for many years thus there is a great deal of literature on this subject. This survey of the literature will be limited to very specific subjects which are relevant to the goals of this study: modeling the adsorption of a toxic chemical in competition with natural background organics. The literature will be reviewed in three parts: mathematical modeling of adsorption, characteristics of background organics and the adsorption of background organics. The first section will review the adsorption modeling literature concentrating on multicomponent applications. The second section will briefly discuss the main characteristics of humic substances, which are the main constituents of the organics present in water sources. The final section will survey studies on the adsorption of humic substances, in equilibrium and column experiments, as well as their modeling. This section will also discuss the limited information presently available on competitive adsorption involving humic substances.

For reviews on the manufacture, physical and surface characteristics, and other applications the reader is referred to Mattson and Mark (1971) and Hassler (1967).

2.2 ADSORPTION MODELING

The modeling of any adsorption process requires two types of information: equilibrium and kinetic data. The former describes the maximum adsorption capacity of the adsorbing material. The latter describes the rate at which the process reaches equilibrium. With the above data, one can formulate mathematical models to describe adsorption processes such as column adsorbers.

2.2.1 Equilibrium Studies and Equilibrium Models

Equilibrium studies and the models describing their results are called isotherms because these studies are carried out at a constant temperature. The experiments are performed by contacting the solution of interest in a set of bottles with different masses of activated carbon (or adsorbent) until equilibrium is reached. At that time, the solution is separated from the carbon and it is analyzed for the contaminant(s) in question. The experiment thus yields the equilibrium liquid phase concentrations as a function of carbon dosage. To eliminate the influence of the initial solute concentration, the data is generally presented as surface or solid phase concentration (obtained by a mass balance) as a function of liquid phase concentration. This relationship is also called the isotherm, and it is described by regressing the observed data to a mathematical model. There are two main types of models: single solute models and multicomponent models. The single solute models are used to describe the adsorption of an individual compound or the adsorption of complex mixtures of compounds described in terms of a gross organic parameter such as TOC or chemical oxygen demand (COD). The latter approach has been used to describe many water and wastewater applications. Multicomponent models are used to

describe multisolute equilibrium experiments in terms of an individual expression for each of the most important solutes.

Peel and Benedek (1980a) found that batch isotherms required substantially longer to reach equilibrium than previously thought. They observed that periods of a month or longer were required to achieve equilibrium for o-chlorophenol in contact with granular activated carbon (GAC).. Figure 2.1 shows the carbon loading in a GAC isotherm as a function of time. Powdered activated carbon (PAC), which adsorbs faster due to the smaller particle radius, required a week to reach equilibrium, while research previously reported in the literature generally allowed up to 8 hours to achieve equilibrium. The adsorption of phenol showed a slightly faster rate of adsorption, but the effect is still significant. Peel and Benedek, therefore, speculated that isotherm duration is the main reason for the large differences reported in the literature for phenol isotherms using Calgon's Filtrasorb F-400. Thus it probably led to substantial underestimation of isotherm adsorption capacity in many applications.

2.2.2 Single Component Isotherm Models

The most common classes of isotherms are shown in Figure 2.2 and they can be represented by:

i) linear $q = L \cdot c$ (2.1)

ii) irreversible $q = L$ (2.2)

iii) favourable $q = g(c), \quad g'' < 0$ (2.3)

iv) unfavourable $q = g(c), \quad g'' > 0$ (2.4)

where q = equilibrium solid phase concentration, grams of solute / g of carbon;

c = equilibrium liquid phase solute concentration, g/cm^3;

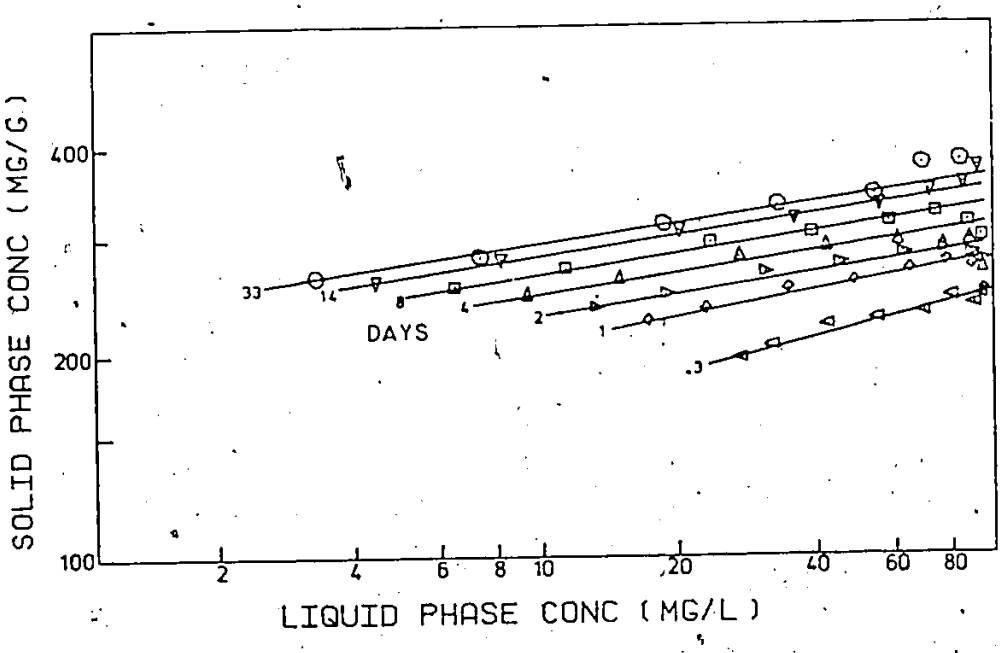

FIGURE 2.1 Apparent o-chlorophenol Loading as a Function of Time for GAC. (after Peel and Benedek (1980a))

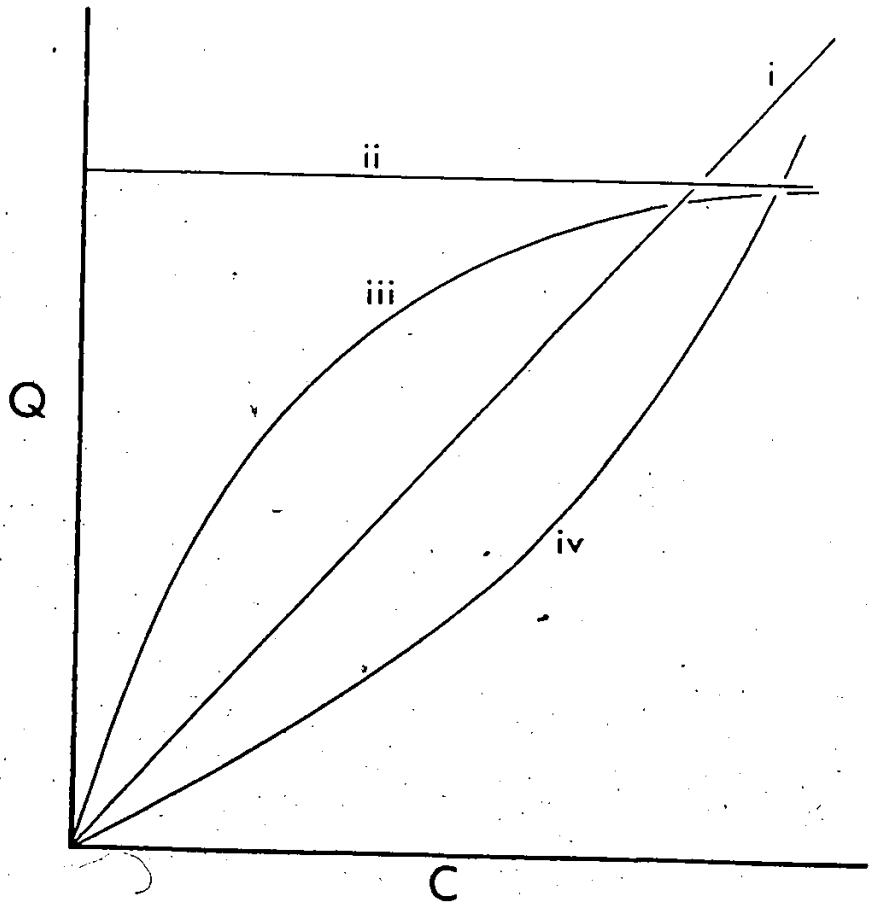

FIGURE 2.2 Common Types of Isotherms In Aqueous Systems.

L = a constant; and,

g = a mathematical expression.

Linear isotherms are the boundary between favourable and unfavourable isotherms. The definition of favourable and unfavourable pertains to the concentration profile within column adsorbers. The favourable isotherm produces a constant size mass transfer zone. The unfavourable isotherm results in a continually expanding mass transfer zone and in this way it utilizes the adsorption capacity inefficiently. The irreversible isotherm is a special case of the favourable isotherm.

The most commonly used expressions to describe isotherms are the Langmuir isotherm and the Freundlich isotherm. The Langmuir expression can be derived theoretically from kinetic and thermodynamic approaches, assuming all the adsorption sites have the same energy of adsorption, that the adsorbed molecules are immobile and that no interactions occur between adsorbed molecules. These assumptions result in a maximum adsorption capacity equal to a monolayer coverage. The Langmuir isotherm model equals

$$q = \frac{QM \cdot b \cdot c}{1 + b \cdot c} \qquad (2.5)$$

where QM = monolayer adsorption capacity, g/g of carbon; and,

b = energy constant, cm^3/g.

The fact that isotherm results can be described by the Langmuir model does not mean the adsorption mechanisms involved are those described by this model. As shown by Sweeney et al (1982) some data can be fitted well by both Langmuir and Freundlich isotherms, and this second isotherm is associated with an exponential distribution of adsorption energies. This model has been shown to fit some isotherms

(Weber and Morris (1964)), but in general, its applicability is limited to small concentration ranges. Thus, as shown by Razzaghi (1976) the results of one experiment may be described by different Langmuir models over different regions.

The majority of liquid-solid adsorption systems can be described by the Freundlich model, probably due to the heterogeneous nature of activated carbon. The expression of this model is

$$q = k \cdot c^n \qquad (2.6)$$

where k and n are constants.

Fritz (1978) and others found that a single Freundlich isotherm could not describe isotherms over several orders of magnitude of the liquid phase concentrations. Fritz et al (1980) avoided the problem by dividing their data into five sections each with its own isotherm. Another approach was to use three parameter models such as those developed by Redlich and Peterson (1959). Jossens et al (1978) and Toth (1971), cited by Jossens et al (1978), also developed three parameter models to describe data covering several orders of magnitude in concentration. Famularo et al (1978) discussed that to obtain an unique set of parameters when applying the Jossens et al (1978) three parameter model, data covering five orders of magnitude is required. This drawback is the main reason for the limited use of the three parameter model.

In order to reduce the number of equilibrium experiments required for the design of adsorbers, several researchers have developed adsorption theories which can predict the adsorption of organic compounds based on their physical properties and on characteristic adsorption curves. These curves, which are specific to one activated

carbon, were obtained by correlating the experimental data of many adsorbates with the mathematical models of each theory. The variables of these models are physical characteristics of the adsorbate, such as the solubility, the molar volume, the refractivity, etc. These theories include the Polanyi Adsorption Theory (Manes (1980)), the Net Energy Theory (McGuire and Suffet (1980)), the Solvophobic Theory (Melander and Horvath (1980) and Altshuler and Belfort (1983)) and the Theory of Correspondence (Myers and Sircar (1983)). The principal drawbacks of these theories are that each carbon requires its own characteristic curve, and that not all organics fit the same characteristic curve well, so that often different characteristic curves are required for different types of compounds.

2.2.3 Multicomponent Isotherms

Competitive adsorption isotherm models can be classified into two main groups: predictive models and regression based models. Predictive models are calibrated using only single component isotherms. The regression based models also use the parameters from the single adsorbate isotherms, but in addition they require competitive adsorption data in order to regress the values of the additional coefficients. Thus predictive models are more desirable because they reduce the experimental work required.

2.2.3.1 Predictive Models

Butler and Ockrent (1930) derived the Langmuir competitive adsorption model using the same assumptions as the single adsorbate model

$$q_i = \frac{QM_i \cdot b_i \cdot c_i}{1 + \sum_{j=1}^{NC} b_j \cdot c_j} \qquad (2.7)$$

where, q_i = solid phase concentration of adsorbate i, mole/g;

c_i = liquid phase concentration of adsorbate i, mole/ℓ;

b_i or b_j = constant from the single component Langmuir model for component i or j, ℓ/mole;

QM_i = monolayer solid phase concentration of adsorbate i from single component isotherms, mole/g; and,

NC = number of adsorbates present.

Weber and Morris (1964) showed that this model can successfully predict the competition for bisolute mixtures of DBS (dodecyl benzene sulfonate)- phenol and DBS-nitrobenzene. Murin and Snoeyink (1979) found this model was inadequate for describing the competition of 2,4-dichlorophenol and 2,4,6-trichlorophenol over a wide range of concentrations. Even using a semi-empirical approach, the model was only adequate at one of the pH levels tested. Crittenden et al (1980) found this model adequate for the prediction of p-nitrophenol-O-bromophenol systems. Radke and Prausnitz (1972) pointed out this model only obeys the laws of thermodynamics when the QM's for all the adsorbates are equal.

Jain and Snoeyink (1973) derived a Langmuir type empirical model for bisolute systems that assumes some adsorption sites are only available to the stronger adsorbing compound. The exclusiveness is attributed to pore size exclusion of the adsorbate or chemical specificity of the sites. The magnitude of the single component monolayer loading, QM, determines which is the stronger adsorbing compound, and the non-competitive sites are proportional to QM_1-QM_2. Letting solute #1 be the strongest adsorbing compound the model is as follows:

$$q_1 = \frac{(QM_1 - QM_2) \cdot b_1 \cdot c_1}{1 + b_1 \cdot c_1} + \frac{QM_2 \cdot b_1 \cdot c_1}{1 + b_1 \cdot c_1 + b_2 \cdot c_2} \qquad (2.8)$$

$$q_2 = \frac{QM_2 \cdot b_2 \cdot c_2}{1 + b_1 \cdot c_1 + b_2 \cdot c_2} \qquad (2.9)$$

where QM_1, QM_2, b_1 and b_2 are obtained from the single component isotherms; and $QM_1 > QM_2$. This model was tested with several bisolute systems consisting of neutral and anionic p-nitrophenol, neutral and anionic p-bromophenol and anionic benzene sulfonate. The predictions were very good for the mixtures of nitrophenol and bromophenol, which are similar compounds with similar single solute isotherms. And the predictions involving benzene sulfonate were rather poor. For nanomolar and micromolar chlorophenol experiments Murin and Snoeyink (1979) found this model's predictions to be satisfactory in a limited number of cases. In spite of its limitations, this model was the first attempt to model the non-competitive sites. The existence of such sites has been suggested by Weber and Morris (1964) as an explanation for the total molar solid phase loading of a mixture exceeding the loading of the strongest adsorbing compound in a single solute experiment.

The ideal adsorbed solution model (IAS) was derived by Radke and Prausnitz (1972) based on thermodynamics. This model has the following assumptions: a) the liquid solutions are dilute; b) the adsorbent is inert and has a specific surface that is identical for all adsorbates, and c) the adsorbed phase forms an ideal surface. This model is applicable to as many solutes as desired and its general form is

$$q_T = \Sigma\, q_i \qquad (2.10)$$

$$z_i = q_i / q_T \qquad (2.11)$$

$$1 = \sum_{i=1}^{NC} z_i \qquad (2.12)$$

$$1 / q_T = \sum_{i=1}^{NC} (z_i / q_i^o) \qquad (2.13)$$

$$\frac{\pi A}{R T_a} = \int_0^{c_i^o} (q_i / c_i)^o \, dc_i^o \qquad (2.14)$$

$$q_i^o = f(c_i^o) \qquad (2.15)$$

$$c_i = c_i^o \cdot z_i \qquad (2.16)$$

where, c_i = liquid phase concentration of the solute in the mixture, moles/ℓ;

q_i = solid phase concentration of solute i , moles/gram of carbon;

z_i = adsorbed phase mole fraction of solute i;

q_T = total molar concentration on the activated carbon, moles/g;

A = surface area of the adsorbent;

π = spreading pressure;

R = universal gas constant;

T_a = absolute temperature;

c_i^o = liquid phase concentration of solute i when that solute adsorbs alone at the same temperature and spreading pressure as those of the mixture, mole/ℓ;

q_i^o = solid phase concentration of solute i when that solute adsorbs alone at the same temperature and spreading pressure as those of the mixture, mole/ℓ;

$f(c_i^o)$ = single solute isotherm model; and,

and NC = number of solutes in the mixture.

This model is very flexible since the single solute isotherms, equation 2.14, can have many mathematical forms. However, since q_i^o is part of

the integral in equation 2.14, the equation of the single solute isotherm greatly affects the computational effort involved. If the integral has to be solved numerically, this model requires substantial computational resources. Consequently, it is highly desirable to use a single solute model that results in an analytical solution, such as the Freundlich model.

Jossens et al (1978) explained that the Freundlich isotherm should not be used as it is thermodynamically unsound because at low concentrations it does not reduce to Henry's law, and the solid phase concentration does not reduce to zero at zero liquid phase concentration. This introduces errors into the evaluation of the integral in equation 2.14. Singer and Yen (1980) showed that this error is small, thus it seems practical whenever possible to represent the single solute data by the Freundlich isotherms. In such cases, the IAS model for a binary solution isotherm reduces to two simultaneous non linear equations that can be solved by Newton's method. And for the column simulations using the film-surface diffusion model, the IAS equations are solved explicitly.

Radke and Prausnitz (1972) predicted very well most of their acetone-propionitrile and p-cresol-p-chlorophenol data. However, some significant deviations were observed for the latter mixture and in order to better simulate the data, the authors proposed a correction factor. The single component isotherms chosen by the above authors were the rather elaborate Newman's 3 and 5 parameter equations which could be integrated analytically.

Jossens et al (1978) used the Toth three-parameter model in their application of the IAS theory. Their predictions were excellent

for five bisolute systems consisting primarily of phenolics. However, they were somewhat poorer for the 2,4-dichlorophenol / dodecyl benzol sulfonic acid system, which was the most dissimilar pair. Fritz and Schlunder (1981) analyzed the same binary systems with equal success using a IAS routine based on a multirange Freundlich isotherm.

Singer and Yen (1980) found that the isotherms of phenol-2-methylphenol and phenol-2,6-dimethylphenol mixtures could be predicted very well by Freundlich-based IAS models. A Langmuir-based IAS model was also tested but it yielded poor predictions for the second binary system. Thacker et al (1981) found large discrepancies between the IAS predictions and their 3,5-dichlorophenol-3,5-dimethylphenol. This was somewhat surprising as excellent predictions for phenolics were reported in the literature. To compensate for the discrepancies, Thacker et al (1981) replaced equation 2.16 by

$$c_i = r_i \cdot c_i^o \cdot z_i \qquad (2.17)$$

where r_i is the average ratio of experimental to predicted solution concentration for species i. Fukuchi et al (1980) described that the use of the IAS model is somewhat restricted due to adsorbed phase non idealities observed in experiments. Yonge and Keinath (1984) showed that the IAS model predicted poorly the competition in several binary mixtures of phenolics.

Razzaghi (1976) developed a model analogous to that of Jain and Snoeyink (1973) based on Freundlich isotherms. The general version of the model is:

$$q_i = (1-w_i)\, k_i\, c_i^{n_i} + w_i \left(c_i / \sum_{j=1}^{NC} c_j\right)^{n_i} \cdot k_i \cdot c_i^{n_i} \qquad (2.18)$$

where w_i is the fraction of the overall capacity of compound i which is involved in the competition. The values of w_i can be predicted using

the Jain and Snoeyink isotherm at low carbon loadings. This model was tested for several binary mixtures of soluble, high molecular weight organics and different chemical nature. These included pepsin, bovine serum albumin, maltose and dextran (MW = 10,000, 70,000 and 2,000,000) and two lignin sulfonate fractions. Comparisons with the Jain and Snoeyink model yielded similar predictions at low loadings and superior predictions at higher loadings.

DiGiano et al (1978) have presented a model derived using the IAS model with some simplifying assumptions, which has been named SCAM. This model which is based on the Freundlich isotherm assumes the single solute isotherms of all the components are equal, and it utilizes mean coefficients k' and n' when this assumption is not true. The general form of SCAM is:

$$q_i = k'^{(n'-1)/n'} \cdot (k_i \cdot c_i^{n_i})^{1/n'} \cdot \left(\sum_{j=1}^{NC} ((k_j/k') \cdot c_j^{n_j})^{(1/n')(n'-1)} \right) \qquad (2.19)$$

where $n' = \left(\sum_{j=1}^{NC} n_j \right)/NC$;

$k' = \left(\prod_{j=1}^{NC} k_j \right)^{(1/NC)}$; and,

NC = number of components.

The above authors compared the predictions by SCAM and IAS for some of the data generated by Fritz (1978) and found that in most cases involving low concentrations, SCAM gave comparable predictions.

Yonge and Keinath (1984) developed ISIAS (improved simplified IAS) model by replacing the k_i terms in SCAM by k_i/p_i in order to account for non-ideal adsorption behaviour. The values of p_i were initially obtained by non-linear least squares regression of data equilibrium studies involving four binary solutions of phenolics. Then they were successfully correlated with a ratio of the solubilities, thus

making ISIAS a predictive model. The values of p_i were greater than one, thus this model always predicts loadings equal to or lower than SCAM.

The above models were developed to satisfy several goals, such as adherence to thermodynamics and mathematical simplicity. However, the main reason for the development of most models is deficient predictions of earlier models. This has led to the development of models of competitive isotherms calibrated via regression.

2.2.3.2 Regression Based Models

Fritz and Schlunder (1974) proposed the following very general model:

$$q_i = \frac{a_{io} \cdot c_i^{b_{io}}}{d_i + \sum_{j=1}^{NC} a_{ij} \cdot c^{b_{ij}}} \qquad (2.20)$$

where a_{io}, b_{io}, d_i, a_{ij} and b_{ij} are regressed coefficients. This model can be reduced to the Langmuir or the Freundlich models, thus some of the constants are calibrated from the single solute isotherms. The remaining components must be obtained via regression. For example, for a bisolute system with the individual components having Freundlich isotherms, six constants must be regressed. This permits a great deal of adjustment by regression techniques, so the simulations are excellent as shown by the above authors for many phenol-p-nitrophenol solutions. This model was also found superior by Balzli et al (1978) for a 2-butanol-t-amylalcohol system and for a system involving the same compounds plus phenol.

Fritz and Schlunder (1981) also used their model to successfully simulate four binary mixtures, which the IAS model could not predict

very well. Fukuchi et.al (1980) found the above model could describe well the adsorption of phenol-benzoic acid mixtures.

Mathews and Weber (1980) developed a competitive isotherm based on the Radke and Prausnitz (1972) three parameter isotherm. It is as follows:

$$q_i = \frac{\beta_i \cdot (c_i/\eta_i)}{1 + \sum_{j=1}^{NC} a_j \cdot (c_j/\eta_j)^{\alpha_j}} \qquad (2.21)$$

where β_i, a_j and α_j are parameters of the Radke and Prausnitz single solute models; and η_i are parameters obtained from the regression of competitive isotherm data.

In conclusion, in spite of a substantial effort to model competitive isotherms, there has been only limited successes due to the complexity of the problem and to our present lack of a good understanding of adsorption. The models have not been general enough to describe all the available data. Thus data has been represented by the best fitting model, and this has led to the development of many models.

2.2.4 Kinetic Modeling

As discussed in section 2.2, the kinetic data is one of the two basic types of information required to model and design adsorbers. These data can be obtained from a wide variety of experiments, but they all involve the monitoring of the changes in solute concentration caused by a given mass of adsorbent. Modeling the adsorption rate is a subject that has received considerable attention over the last 30 years. The discussion herein will concentrate on the most pertinent recent studies. For more exhaustive reviews, the reader is referred to Weber and Chakravorti (1974), Crittenden (1976) and Peel (1980) among others.

The mass transfer from the bulk liquid onto the surface of the

adsorbent takes place in three main steps:

i) Transfer across the external liquid film that surrounds the particle;

ii) Transfer from the liquid onto the surface of the adsorbent (adsorption step);

iii) Intraparticle diffusion.

Most of the early research concentrated on models which made many simplifying assumptions in order to solve the model analytically. These assumptions included: negligible mass transfer resistance, a single overall rate expression, the selection of the liquid film mass transfer as the controlling step, the representation of the intraparticle mass transfer by a linear or quadratic driving force, linear isotherms, irreversible isotherms, and constant pattern adsorption waves within column adsorbers. Some of these models were successful in predicting the performance of adsorbers under certain conditions, but they failed under other conditions. For example, Fritz et al (1980) found that in modeling a column receiving a 1 mmole/ℓ phenol solution, he did not require intraparticle resistances to obtain good predictions, the film resistance sufficed.

Due to the shortcomings of the simplified models, the more recent models reduced the number of assumptions. This progress has been aided by the increased availability of computers which are required for the numerical solution of these models.

Present models assume that the rate of adsorption is not the rate controlling step, and that adsorption is controlled by either the liquid film or the intraparticle diffusion. The two main types of rate models presently used differ in their interpretation of the

intraparticle diffusion. The surface diffusion or homogeneous solid surface diffusion (HSSD) model, treats the carbon particle as a solid. The adsorbate adsorbs at the surface of the particle and migrates along the pore walls to the interior of the particle by surface diffusion. The relationship between the liquid and the solid phase concentrations at the outer surface of the particle is described by the isotherm. The pore diffusion or heterogenous diffusion model considers that the carbon particle is porous and the solute is transported to the interior of the particle by diffusing through the liquid that fills the pores. The solute can then be adsorbed at any point along the radial direction, so the solid - liquid boundary condition, represented by the isotherm, is not localized.

The basic assumptions of these models are that:

i) adsorption is not the rate controlling step

ii) the apparent diffusion coefficients are independent of concentration and radial location

iii) the bulk flow terms can be neglected as the concentrations are dilute

iv) the carbon particles are spherical.

The resulting differential mass balances for the particles are:

Pore diffusion

$$\rho_c \frac{\partial q'}{\partial t} + \varepsilon_p \frac{\partial c'}{\partial t} = D_p \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c'}{\partial r} \right) \right\} \qquad (2.22)$$

Surface diffusion

$$\frac{\partial q'}{\partial t} = D_s \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q'}{\partial r} \right) \right\} \qquad (2.23)$$

where ρ_c = particle density of the adsorbent, g/cm^3;

q' = solid phase concentration, g/g;

t = time variable, sec;

ε_p = internal porosity of the particle;

c' = liquid phase concentration within the pores, g/cm^3;

D_p = apparent pore diffusion coefficient, cm^2/sec;

r = particle radial variable, cm; and,

D_s = apparent surface diffusion coefficient, cm^2/sec.

Recently Fritz et al (1981), among others, considered the combined pore and surface diffusion model, because the pore diffusion model was inconsistent in some applications. The apparent pore diffusivity was defined by Wheeler (1951) as

$$D_p = \frac{\varepsilon_p \cdot D_l}{\nu} \qquad (2.24)$$

where D_l = free liquid diffusivity, cm^2/sec; and,

ν = tortuosity factor, which is the mean ratio of the actual path length travelled by an adsorbing particle to the radial distance travelled.

Thus the tortuosity factor, which has been reported in Satterfield (1970) to range from 2 to 4, should never be less than one. Yet different studies have found some applications where D_p was larger than or equal to D_l, and this faster transport was attributed to surface diffusion.

In spite of noticing this effect, some researchers such as Liapis and Rippin (1977) have used the regressed values of the pore diffusion even when they exceeded the free liquid diffusivity. Others, such as Fritz et al (1980), used the combined model with a fixed tortuosity factor, thus fixing D_p and regressing the information to find

D_s. Komiyama and Smith (1974) found that the greater importance of surface diffusion occurred in situations of low liquid concentrations and high adsorptivity. Unfortunately, there are presently no methods of measuring the solid and liquid phase concentrations along the radius of a particle. Thus, it is impossible to directly measure the influence of each mechanism. The choice of the model used is somewhat arbitrary since in most cases both models can be regressed to fit single solute kinetic data.

Famularo et al (1978) were unsuccessful in modeling their batch kinetic data using the surface diffusion model even when they included a concentration dependent diffusivity. To describe the data they developed a micropore / macroshell concept as a representation of the bimodal pore size distribution in carbon particles described by Keinath (1968). Their model described the intraparticle mass transfer by two linear resistances in series. Famularo et al (1978) calibrated their model using batch tests, but found it necessary to recalibrate it to represent their column data.

In work parallel to that of Famularo et al (1978), Peel and Benedek (1980b,1981) and Peel et al (1981) observed during batch kinetic studies that adsorption frequently occurs by two distinct mechanisms. One mechanism was fairly fast while the other was significantly slower, thus the name: slow adsorption phenomena. The slowness was hypothesized to be caused by chemical or pore size restrictions. The fraction of the overall adsorption capacity attributed to the slow mechanism was generally found to be proportional to the molecular size of the adsorbate. The main contribution of this research was that it identified the need of longer kinetic tests to observe both these

mechanisms and accurately model adsorption. Based on their observations two dual rate models were developed.

The first model presented in Peel et al (1981) and in Peel and Benedek (1981) is an extension of the surface diffusion model where the slow adsorbing pores are considered as a sink. The slow adsorption rate expression is a linear driving force. Peel and Benedek (1980b) also developed a second more computationally efficient model, based on the average solid phase concentrations. The rapid adsoprtion was described by a quadratic driving force and the slow adsorption mechanism is again represented as a linear driving force. These models with their longer calibrating tests were able to predict well the column breakthroughs of several waters and wastewaters. These predictions were particularly good in describing the observed long term removals.

Weber and Liang (1983) presented a dual intraparticle resistance version of MADAM, one of the most often used homogeneous solid diffusion modeling computer programs. This model is very similar to the one presented by Peel et al (1981). In this model the slower mechanism is conceptualized as occurring within small imaginary spheres distributed throughout the carbon particle, and the driving force of the microspheres is described by a second Laplacian term.

Summarizing, the pore and surface diffusion models and their combination are presently widely used. And in many cases, it has been shown that an additional intraparticle resistance is required to model the observed data.

2.2.5 Multicomponent Batch Kinetics

Multicomponent batch kinetics tests have received very limited attention. The vast majority of the research on the dynamics of the

adsorption of competing organics has been limited to column studies. Some of the column investigations have been strictly experimental in nature. The remaining competitive column research has concentrated on the prediction of adsorber performance using mathematical models calibrated using single component batch kinetics (Famularo et al (1978), Crittenden et al (1980)).

Multicomponent kinetic models are composed of duplicates of the same differential mass balances as single solute models, one set for each solute. The sole competitive aspect of these models is the adsorption step which is described by the competitive isotherms. These models presume that the mass transfer rates of the individual solutes are independent of each other, thus the values of the mass transfer coefficients can be regressed from the single solute kinetic tests. This is a very attractive assumption because it avoids additional tests in an experimental program that already involves NC single solute isotherms, at least one competitive isotherm plus NC kinetic tests, where NC is the number of components studied. Multicomponent batch kinetic tests are the additional step required to verify the above assumption, and if necessary, they can be used to calibrate the models so as to describe the dynamic interactions.

Weber and Morris (1964) reported one of the first competitive kinetic experiments using binary systems. Their experiments showed the presence of additional solutes reduces the mass transfer rates of all the compounds studied. The magnitude of the reduction is a function of the molecular sizes of the competing species. Since no attempt was made to mathematically model these experiments, it is impossible to determine if the observed decreases could have been predicted using the pure

solute calibrated models.

Mathews and Weber (1980) studied the batch kinetics of phenol-p-bromophenol, phenol-p-toluene sulfonate and phenol-dodecyl benzene sulfonate (DBS). The film-surface diffusion model in conjunction with their own isotherm was used to simulate these tests. The predictions were very good for the first two systems which have very similar values of the diffusivity coefficient, although one had different adsorption characteristics. In the last system, the diffusivity coefficients differed by a factor of 14 and the predictions were rather poor. This is not surprising since Fritz and Schlunder (1981) had similar results with a 2,4-dichlorophenol - DBS mixture. The discrepancies were attributed to diffusional interactions, Mathews and Weber (1980) improved the simulation by adjusting the film diffusion coefficients.

Liapis and Rippin (1977) developed two competitive adsorption kinetic models, one describing the internal mass transfer resistance as pore diffusion process and the other as surface diffusion. Since typical applications involve dilute solutions, these researchers assumed the individual solutes diffuse independently. They also presented the modified version of the models required to account for diffusion interactions that might be required at high concentrations of dissimilar components. The dilute solution models were calibrated using a competitive batch kinetics test and they predicted with great accuracy the column breakthroughs for a butanol-2-t-amyl alcohol solution (Balzli et al (1978), Liapis and Rippin (1978)). The success of this model is at least in part due to the calibration using a competitive kinetic test, but refraining from conducting single component kinetics also

leads to a loss of information on the diffusion interaction.

Mathews and Su (1983) predicted the competitive batch kinetics of naphthalene and phenol using the homogeneous solid diffusion model. The mass transfer coefficients were regressed from individual solute batch kinetic tests. The IAS model and Mathews and Weber's 4 parameter competitive isotherm were tested as the equilibrium expressions. The simulations of the competitive batch kinetic tests were excellent for phenol, but they consistently overestimated the naphthalene removals. The predictions with the IAS model showed large deviations from the data, while those calculated using the other equilibrium model deviated to a lesser degree. However, since the competitive isotherm data was not presented, one cannot ascertain to what degree these errors were due to inaccuracies in the isotherm model and due to dynamic solute interactions.

Fritz et al (1980) and Fritz et al (1981) conducted a thorough study of competitive batch kinetics and their modelling using pore diffusion and surface diffusion models. They showed that although both models have very similar concentration histories for single compound kinetics, in competitive kinetics these models can predict widely different results. Six batch kinetic runs were conducted with different binary mixtures. In half of the cases the predictions were very good, and the pore diffusion model predictions were usually slightly better than those by the surface diffusion model. Some of the remaining systems involving p-nitrophenol and phenol did not yield such accurate predictions although both compounds have similar diffusion rates. In order to improve the less successful predictions, these experiments were used to calibrate a surface diffusion model with cross diffusion terms.

This new model was then used to predict competitive column runs (Fritz et al (1981)).

Therefore, the literature indicates that in most applications involving solutes with similar values of the diffusivity, good predictions are possible assuming that there are no diffusional interactions. And when the diffusivities are significantly different, dynamic interactions should be considered.

2.2.6 Multicomponent Column Modeling

Crittenden (1976) and Crittenden et al (1978) investigated the adsorption of phenol-dodecyl benzene sulfonate (P-DBS) and phenol-p-toluene sulfonate (P-PTS) in columns. Their simulations used a liquid film-surface diffusion model in conjunction with the Mathews and Weber (1980) competitive isotherm, which were calibrated using batch tests. The P-PTS system was modeled fairly well overall, but the predictions were poor in some areas. The predictions for the P-DBS systems, and the phenol in particular, are rather poor. This was attributed to diffusional interactions due to the large difference in the solid diffusivities, $D_{phenol}/D_{DBS} = 7.5$. This was demonstrated by the significantly improved prediction generated by using the value of the smallest diffusion coefficients and its corresponding film transfer coefficients for both compounds. It should be noted that Mathews and Weber (1980) could not predict accurately the batch kinetic test of the same mixture.

Liapis and Rippin (1978) presented their predictions for the 2-butanol-t-amyl alcohol breakthrough based on a film-pore diffusion model. This column model, which also includes axial backmixing, was calibrated by the competitive batch kinetic tests mentioned in the

previous section. The predictions underestimate the size of the overshoot of the weaker adsorbate, but are otherwise excellent. The accompanying error analysis showed that the entire error could be accounted for by the inherent error of the mass transfer correlations used to calculate the film mass transfer coefficient. The high quality of these simulations is the result of several factors. Firstly, the calibration via competitive kinetics compensates for possible cross diffusion effects that the model does not take into account. Secondly, $D_{p1}/D_{p2} = 0.567$, therefore cross diffusion effects will not be very significant.

Famularo et al (1978) developed a model which represents the internal particle mass transfer by two linear resistances in series. The model utilizes the Myers three parameter isotherms in conjunction with the IAS theory to describe the multicomponent equilibria. The model was calibrated using single adsorbate batch kinetics, and one of the single component column runs. The prediction for the equimolar p-nitrophenol-phenol feed was good.

Merk et al (1980) is the last of a series of papers based on the doctoral studies of Merk and Fritz. It displays column predictions by film-pore diffusion and by the film-surface diffusion models developed and calibrated in Fritz et al (1980) using single solute batch kinetic tests. The bicomponent equilibria are represented by the IAS theory using a set of different Freundlich isotherms to describe different concentration ranges. The predictions for the three equimolar feed p-nitrophenol p-chlorophenol systems are very good but their accuracy decreases somewhat with increasing column length and higher influent concentrations. This implies the errors are related to higher column

loadings and they are the results of diffusional interactions. The predictions of the p-nitrophenol-phenol column runs show greater error, which led these researchers to use a solid diffusion model with cross diffusion terms. This latest model significantly improved their predictions.

Crittenden et al (1980) applied the film diffusion - homogeneous surface diffusion model to predict the adsorption of p-nitrophenol and p-bromophenol on a column packed with Duolite A-7 resin. Equilibrium was described by the competitive Langmuir isotherm and diffusion interactions were assumed to be negligible. The model was calibrated using a column run with an equimolar solution of the above compounds. This run was also used to recalibrate the isotherm parameters. The model successfully predicted the breakthrough concentrations of columns fed one of the above compounds until saturated, followed by a bisolute feed. This agreement is not surprising considering the method of calibration and the relatively close values of the diffusion coefficients.

Thacker et al (1981) successfully predicted bisolute column breakthroughs for 3,5-dimethylphenol and 3,5-dichlorophenol in beds of three different activated carbons. They used liquid film-surface diffusion model developed by Crittenden et al (1980) with a different isotherm. Multicomponent equilibrium was described by the IAS model based on the Myers three parameter isotherm which was then modified by a constant to improve its prediction capacity.

Sheindorf et al (1983) developed a pore diffusion model with a constant wave front propagation for the column adsorber. This model was calibrated using single component batch kinetic tests and it was tested

by simulating column runs with single component, binary and ternary feeds. The single compound predictions were fair, but unable to predict the slow adsorption tailing effect for phenol. The binary and ternary predictions were poor. The authors suggest that the inaccuracies might be due to their simplified mathematical analysis, concentration dependent diffusivities and/or cross diffusion effects.

In light of the fairly good predictions it should be noted that the majority of these competitive column studies are rather limited in scope. The majority utilize binary systems comprised of equimolar solutions of compounds with similar structures. In addition, the diffusion coefficients of most column systems differ by a factor of two. The biggest exception was the dodecyl benzene sulfonate - phenol system studied by Crittenden (1976) $D_{sp}/D_{s_{DBS}} = 7.5$, and it yielded the poorest prediction. The results are a confirmation of the findings from the batch kinetic tests.

2.3 DESCRIPTION OF HUMIC SUBSTANCES

As discussed earlier, the background organics present in all water sources are mainly humic substances, but they are also found in soils, rock and the marine environment. As such, they have been extensively studied by scientists of various disciplines and there is a great deal of literature on this subject. This review will be limited to a very general description of these substances and some of their characteristics that are relevant to this study. For a more detailed discussion of the humic literature, the reader is referred to Schnitzer and Khan (1972), Gjessing (1976), Christman and Gjessing (1983), and Aiken et al (1985).

Humic materials are an amorphous group of hydrophobic, acidic

substances with molecular weights ranging from a few hundreds to several tens of thousands. These compounds are the result of the microbial breakdown of organic matter, and as such are resistant to microbial degradation. These substances are classified based on their solubility: humic acids (HA) are only soluble in alkaline solutions, fulvic acids (FA) are soluble in both alkaline and acidic solutions and humins are insoluble in acid or basic solutions. These fractions are structurally similar, but they differ in their molecular size, elemental content and functional group content. Black and Christman (1963) found that the humic substances in natural waters are approximately 80 to 90 percent fulvic acid, because of their higher solubility. Schnitzer and Khan (1972) discussed that the FA fraction has lower molar mass but a higher content of oxygen-containing functional groups per unit mass.

Malcolm (1985) explained that aquatic humic substances differ substantially from soil humic substances. For example, in soils the HA to FA ratio is approximately 3:1, while in aquatic sources it equals 1:9. In addition, aquatic humics from groundwater, lakes, streams and estuaries also have some differences, such as the percentage of the TOC which is hydrophobic (Thurman (1985)). These differences are presumably caused by the different origins and formation mechanisms of the humic substances.

Malcolm (1985) reported that the dominant structure of stream humic substances are primarily aliphatic and that only 15 to 30 percent of the carbon in these substances form aromatic groups. Oxygen-containing functional groups substitute every third or fourth carbon atom on the main aliphatic structure. For stream fulvic acids the major functional group is carboxyl, with minor amounts of phenolic

and methoxyl. The molecules of stream humic acids contain phenolic, methoxyl and carboxyl functional groups as well as aliphatic side chains of 6 to 10 carbon atoms in length. Due to the complexity of the humic macromolecules, there is continuing work to identify all of their features. The work of Liao et al (1982) is an example of this type of research, the degradation products of humic matter are identified and the origin of these products is hypothesized.

Humic substances consist mainly of carbon, oxygen, hydrogen, nitrogen, phosphorous and sulfur, the percentage of each element being dependent on the source of the humics. The carbon content of these aquatic humics ranges from 40.6 percent (Black and Christman (1963)) to 62.7 percent (Thurman and Malcolm (1981)) and average approximately 50 percent.

There is substantial disagreement as to the molecular weight of humics. This is partly due to the use of many different methods, each measuring different characteristics of the macromolecules (Schnitzer and Khan (1972)). Some techniques such as cryoscopy and osmotic pressure measurements yield number average molecular weights, while viscosity and ultracentrifugation give mass average molecular weights. Gel permeation chromatography, ultrafiltration and small angle x-ray scattering actually measure molecular size and they must be calibrated using compounds of known molecular weight. Different techniques may yield widely different values of the molecular weight of the same substance. Wershaw and Aiken (1985) reported that every technique has some limitations, thus it advisable to use more than one technique. Table 2.1 shows some of the molecular masses reported in the literature.

In water treatment humics are measured in terms of their total

TABLE 2.1 Molecular Weights of some Aqueous Humics

REFERENCE	SOURCE OF HUMICS	METHOD OF MEASUREMENT	MOLECULAR WEIGHTS		
Wilson and Weber (1977)	Oyster River New Hampshire	Cryoscopic Determination	MW_N = 626		
Davis et al (1981)	Lake Greifensee Switzerland	Gel Chromatography	500<	<500	42.5%
			4000<	<4000	39.5%
					18.0%
Andersen and Maier (1979)	Mississippi River	Membrane Separation	1000<	<1000	50.0%
				$<10^6$	50.0%
Veehstra and Schnoor (1980)	Iowa River	Gel Chromatography		<1000	20-40%
				<2000	70-90%

organic carbon (TOC) concentration, which represents about 50 percent of the mass. Because low level TOC measurements are time consuming, the concentration of humics is often measured using ultraviolet absorption and TOC calibration curves. The ultraviolet spectra generally lacks characteristics peaks, thus any wavelength can be chosen. Dobbs et al (1972) and Peel (1980) used 254nm, Weber et al (1980) used 250nm, Randtke and Jepsen (1982) used 300nm.

2.4 ADSORPTION OF HUMICS

The removal of humic substances by activated carbon did not receive much attention previous to the discovery of the capacity of forming trihalomethanes during the 1970's. As reported in Suffet and McGuire (1980), since then a considerable number of pilot scale column tests have been conducted at different locations.

The main benefit of these tests was the achievement of an overall knowledge of how adsorbers would perform. That is, the type of breakthroughs observed, the adsorption capacities for humics and trihalomethanes of the different brands of carbon, etc. However, little basic research has been conducted into the conditions of adsorption, the modeling of column adsorbers for drinking water applications, and the competitive adsorption of humics. The following subsections will discuss this research.

2.4.1 Adsorption Capacity of Humics

Peel (1980) tabulated the isotherms reported for several natural waters and for humics solutions, and a large variation was apparent. Peel and Benedek (1980a) found that most previous researchers conducted their isotherm tests for too short a duration, and as a result underestimated the adsorption capacities. This is particularly critical

in the adsorption of humics because, due to their large molar size, diffusion is very slow. Peel (1980) speculated that since small sized adsorbates, such as phenol and o-chlorophenol, required about one month to reach equilibrium with GAC, humic material would take much longer, perhaps even years. This was confirmed through simulations by Randtke and Snoeyink (1983). Thus it is impractical to use GAC for isotherm studies of natural waters, thus PAC should be used.

McCreary and Snoeyink (1980) conducted a large number of isotherms using humics of different sources which showed: a) the adsorption capacity of a fulvics solution increased with decreasing pH; b) increasing PO_4 buffer strength at pH=7.0 increased the adsorption capacity; c) the isotherms of fulvics of different sources were widely different; d) the different fractions of each source showed a decreasing capacity with increasing molecular weight; e) the unfractionated humics tended to behave similarly to the lower molecular weight fraction despite that the latter represented a small fraction of the overall mass. The last two observations might be the result of the slower kinetics of the higher molecular weight organics and the 7 day duration of the isotherms.

Lee and Snoeyink (1980) and Lee et al (1981) conducted a very extensive study of the adsorption of several HA and FA using nine brands of activated carbon. Their findings are as follows. First, alum coagulation tripled the adsorption capacity of peat fulvic acid, and it accelerated the kinetics. Second, the adsorption capacity was increased by decreases in pH and by increases in the concentration of alum in the solution. Third, a decrease in the molecular weight of the humics also increased the capacity, contradicting one of the general trends in

adsorption. Fourth, the relative adsorption capacity of humics onto different activated carbons was correlated to the carbon's pore volume in the <70 Å and <400 Å ranges. Some inconsistencies in this approach suggest that different physical chemical properties are also important in the adsorption of humics. And finally, the unfractionated peat fulvic acid isotherm was very similar to that of the MW > 50,000 fraction, although this represents only 9 percent by weight.

Weber et al (1980) observed increases in the adsorption capacity and the rates of adsorption of humic acid in solutions prepared with tap water over those prepared with distilled water. The differences were shown to be caused by ions present in tap water and the authors speculated that the adsorption occurs via a ions - humic - carbon complexation.

Randtke and Jepsen (1982) found that the presence of salts enhanced the activated carbon's adsorption capacity of different humic and fulvic acids. The anions had no visible effect, Na had a slight gradual increase in capacity, while Ca and Mg produced very sharp increases in loading at concentrations of less than one mmole/ℓ.

Weber et al (1983) studied the adsorption of two commercial humic acids and one commercial fulvic acid onto three activated carbons. They found that the adsorption capacity: a) increased in the same order as the predominant pore radius; b) increased with decreasing pH; c) increased with the addition of Na^{+} or K^{+}; d) increased one order of magnitude further when Ca^{+2} or Mg^{+2} was added; and e) remained about the same when Al(III) and Fe(III) were added. This last finding contradicts the finding of Lee et al (1981) on the beneficial effects of alum coagulation as pretreatment. Also, they found that the heterogeneity of

humic substances can lead to substantially different isotherms if conducted by changing different variables. Using the 'fixed initial concentration - variable carbon dosage' method yielded significantly different results from the 'variable initial concentration - fixed carbon dosage' method. Weber et al (1983) also found that decreasing particle size increased the adsorption capacity, but this may at least in part have been a result of the 14 equilibrium times used for GAC.

Weber and Jodellah (1985) found that pretreatment by lime softening and alum coagulation changed the adsorption capacity and kinetics of three humic solutions to a different degree. They concluded that one cannot generalize as the three humics behaved differently. These investigators found that alum coagulation has more favourable effects on the adsorption of humics and they speculated that these improvements were caused by changes to the humics.

2.4.2 Modeling of Columns Treating Humics

The shape of the humics (in terms of TOC) breakthrough curves is one of the most striking results of adsorbers treating natural waters (Figure 2.3). The profile usually starts with an immediate breakthrough of the non-adsorbable fraction. This is followed by a period of varying duration, when the adsorbable organics are completely removed. The actual breakthrough is very gradual, a result of the small diffusivities expected for the large humic molecules. The breakthrough then reaches a point "a", beyond which the breakthrough becomes even more gradual, almost constant. At some point along this tailing part of the breakthrough curve, the column exceeds the adsorption capacity expected from the previously common short duration equilibrium tests. This additional removal was often attributed to biodegradation.

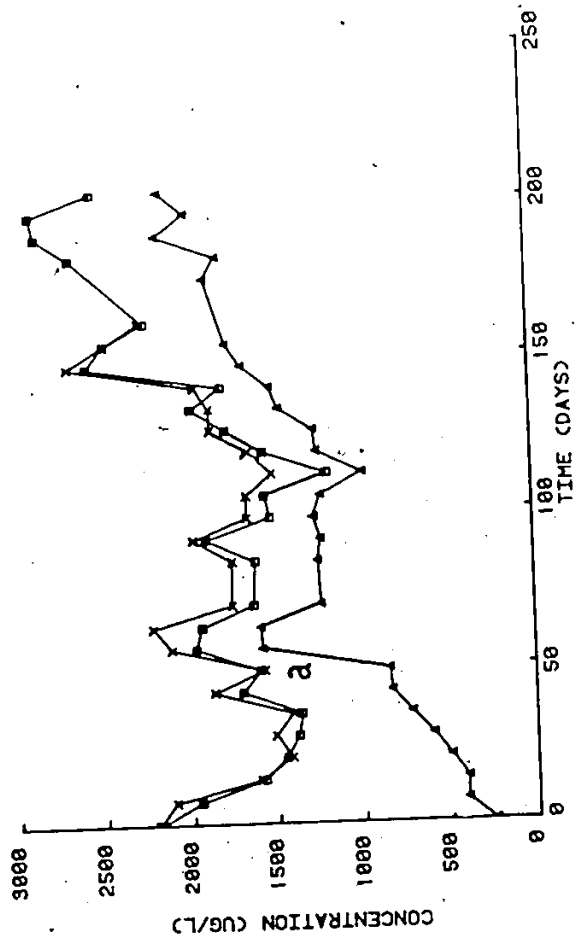

FIGURE 2.3 TOC Breakthrough Curve at a Large Scale System in Cincinnati, OH. (x coagulated and settled effluent; ⊡ sand filter effluent; and, Δ GAC column effluent) (after DeMarco et al (1983))

Weber et al (1980) adequately modeled the adsorption of two humic acid solutions using 12 hr batch kinetic tests. But they found great difficulty in modeling the performance of a laboratory adsorber, due to a gradual breakthrough similar to the one described above. Tests to prove the additional removals were the result of catalytic or biological degradation were inconclusive.

Benedek (1980) and Peel (1980) discussed in great detail the biodegradation - adsorption interactions. As they pointed out, GAC is an excellent medium for bacterial growth. The carbon crevices give sheltered locations for growth, and the adsorption capacity removes toxic compounds that inhibit bacterial growth. Yet most of the background organics in water treatment plants are non-biodegradable. Peel (1980) concluded that there are difficulties in determining the extent of biodegradation at water treatment plant adsorbers, but he showed that the type of breakthroughs often attributed to biodegration were the result of very slow adsorption. This slow adsorption mechanism went unnoticed because batch and kinetic tests were terminated prematurely.

Peel (1980) calibrated his two internal resistance model for treated lake Ontario water with a batch kinetic test lasting 480 hours. Regressing the same information with a single internal resistance model yields a sum of squares of the errors which is 40 percent higher. These models were used to predict the performance of several laboratory adsorbers and in all cases the two internal resistance model was superior. This model excellently predicted the long term removal strictly by adsorption. An important feature of this study is that a single water quality parameter was successfully used to represent a

mixture containing organics of widely different molecular weights.

Lee and Snoeyink (1980) modeled the adsorption of several humic substances with different activated carbons using the homogeneous solid diffusion model. The batch kinetics were modeled adequately in some cases, but the majority showed different degrees of lack of fit. Most of the column adsorber predictions showed a significant deviation from the data. In less than half of the cases the D_s' corresponding to the best fit of the column data was within the 95 percent confidence interval of D_s calculated from the batch kinetics.

Maloney et al (1982) studied the effect of water temperature in pilot scale columns to identify the mechanism of the long term removals. This was done to exploit the different sensitivities to temperature of adsorption and biodegration. They showed these removals were mainly the result of slow adsorption and only a minor part of the observed removals could be attributed to biodegration.

Fiessinger et al (1983) presented the results of one year operation at a 150,000 m^3/day plant which tested six treatment options. These included slow sand filters (with and without preozonation), slow GAC filters (with and without preozonation) and two fast GAC filters treating preozonated water. The comparisons showed that the biologically active slow sand filters could only remove about 10 percent of the TOC while slow GAC filters could remove an additional 15 percent TOC primarily through adsorption. The fast filters removed at least 10 percent more than the slow ones. From these findings, respirometric measurements, and cumulative removal analysis, the above researchers concluded that the slow adsorption mechanism was the primary removal mechanism in the GAC adsorbers.

Weber et al (1983) conducted several small bench scale column runs with solutions of commercial humic acid. During the first set of runs, the breakthrough curves reached the plateau-like region associated with long term removals, within five hours. The same solution was tested with a rapid high pressure mini column as described by Billelo and Beaudet (1983), and it showed that the breakthrough reached the plateau stage in only three minutes. Due to the short elapsed times, it is extremely unlikely that the continuous long term removals could be the result of biodegradation. These results are further proof that the long term TOC removals observed at water treatment plants are largely the result of slow adsorption as first predicted by Peel (1980). Therefore, when modeling solutions of humics or of natural waters, the slow adsorption mechanism should be considered.

Lee et al (1983) showed that the HSSD model could also describe the long term removals observed in adsorbers. However, mass transfer coefficients obtained from batch kinetic tests did not yield good predictions of the column data. The model was calibrated with the column data.

2.4.3 Competitive Adsorption of Humics

Robeck et al (1965) investigated the removal by PAC of several pesticides from spiked distilled water and from river water (COD = 5-35 mg/ℓ). The removals from the river water of dieldrin, a 2,4,5-T ester, lindane and endrin were an order of magnitude lower than those observed from distilled water. The removals of parathion were reduced by about a factor of three. The treatment of river water spiked with lindane, dieldrin and parathion showed that neither lindane nor dieldrin were affected by the presence of the other two pesticides, whereas the

removal of parathion was reduced by a factor of two.

Herzing et al (1977) found in isotherm tests that the adsorption of two odour-causing compounds, 2-methylisoborneol (MIB) and Geosmin, was substantially reduced by the presence of humic materials. This study conducted a very interesting lab scale column run with a MIB distilled water solution as the feed. Initially there was gradual breakthrough of MIB as expected with such a large molecular weight compound, and the introduction of humic acids caused a sharp increase in the effluent profile of MIB. When the feed was changed to distilled water, very little MIB desorbed.

Murin and Snoeyink (1979) reported that the adsorption capacity of 2,4,6-trichlorophenol was reduced by up to 79 percent by the presence of humics. This is a very large reduction considering that this compound is strongly adsorbed.

Chudyk et al (1979) tested the adsorptivity of several activated carbons and synthetic resins for the removal of two different organics from distilled water and humic acid solutions. The first organic was methylisoborneol (MIB), a natural odour causing organic substance frequently found in water treatment plants. The presence of humic acids reduced the adsorptive capacity of two bitumenous coal based activated carbons by 30 to 40 percent. A lignite coal based carbon showed a slight increased MIB adsorption capacity in the presence of humic acids. The second organic was chloroform, the trihalomethane which is found with the highest concentrations, was tested using the lignite coal based carbon and a synthetic resin. Chudyk et al (1979) showed that the chloroform isotherm from a humic acid solution was a fairly typical competitive adsorption isotherm. At low equilibrium chloroform liquid

concentrations it is essentially the same as the pure component isotherm. And as the liquid concentration increased the solid loading increased more gradually than that of the single solute isotherm. For chloroform this difference was approximately 40 percent. Chudyk et al (1979) also found that the carbonaceous resin, Ambersorb XE340, adsorbed chloroform to approximately the same degree as activated carbon, and this capacity was not altered by humic acids. This resin was designed with very small pores especially to avoid removing humic substances in order to retain its adsorption capacity for low molecular weight organics. The above results have been confirmed by numerous investigators such as Chrostowski et al (1983) and Neely and Isacoff (1982).

Weber and Pirbazari (1982, 1983, 1984) investigated the adsorption of several toxic synthetic organics in the presence of humic acids. They found that humic acids adversely affected the adsorption of carbon tetrachloride, benzene, dieldrin and two polychlorinated biphenyls. And the adsorption capacity of p-dichlorobenzene was unchanged by the presence of humic acids. This is the only report of an organic compound whose adsorption to activated carbon is not affected by humics. Considering that the two day equilibrium time utilized is too short for the humic acids to reach equilibrium, some reductions in the p-dichlorophenol capacity may be evident with a more reasonable contact time, such as two weeks. This is likely as Weber and Pirbazari (1983) observed no drop in the capacity to remove carbon tetrachloride when adsorbing it from a humic solution, but the capacity was substantially reduced when the experiment used activated carbon preloaded with humic acids.

All of the studies discussed up to this point in this section did not model the competitive equilibrium experiments. Frick et al (1980) showed that the Rhine River organics substantially decreased the adsorption capacity of p-nitrophenol and vice-versa. These researchers also studied the adsorption of the background organics by modeling the isotherm of such a solution when spiked with a synthetic organic with known adsorption characteristics. The data was regressed using the SCAM model to obtain the Freundlich isotherm constants of the background organics. Frick and Sontheimer (1983) expanded this approach to describe the adsorption isotherms of humic substances which sometimes have odd shapes. Since the organics are mixtures of organics of different molecular weight and composition, this method treats the humics as a mixture of at least three types of organics. Then a multicomponent adsorption model, such as SCAM or IAS, is used to regress the initial concentrations of the pseudo components and their isotherms. The resulting models predict the TOC isotherms of two samples tested: a humic acid solution and a groundwater sample. However, the prediction of the competition of p-nitrophenol with the humic acid was not very good.

Crittenden et al (1984) followed the same approach in analyzing contaminated groundwater, using the IAS model exclusively. The IAS model was first successfully tested for the isotherm of a solution of distilled water spiked with 5 volatile toxic organics. Then, a cis-dichloroethene - groundwater isotherm was analyzed by the pseudo component to calibrate the isotherms of the groundwater. Finally, the IAS method predicted very well the competition between trichloroethene and the groundwater as a confirmation. No indication was given about

the nature of the background organics isotherm, or about how well it is described by this approach in situations with and without competition. The most important point about this investigation is that it addresses the removal of low level toxic organics by adsorbers in the presence of humics, i.e., the drinking water plant problem.

2.4.4 Kinetics of Toxic Organics in the Presence of Humic Substances

Weber and Pirbazari (1982, 1983, 1984) conducted batch kinetic tests for several toxic organic compounds from both distilled water and humic acid solutions. The data were analyzed by comparing the mass transfer coefficients obtained by regressing only the toxic organic data of both experiments to a single component model. In most cases, at least the film mass transfer coefficient of the distilled water had to be readjusted to describe the humic acid run. Due to this rather simplistic analysis, it is impossible to identify the source of the required readjustment. It could be changes of the isotherm (i.e., using a competitive isotherm) or changes in the mass transfer coefficients. To avoid these readjustments, the kinetics of the humic acid and synthetic organics should have been modeled simultaneously including the competitive interactions between the two compounds. This last approach is the one utilized in this thesis.

2.4.5 Removal of Toxic Organic Substances at Drinking Water Plant Adsorbers

As mentioned in Section 2.4, in the last decade many bench scale and pilot scale tests have been conducted in the U.S. to evaluate the performance of GAC adsorbers for removing background organics, trihalomethanes and various synthetic organic compounds found in natural waters. These tests investigated the effects of process variables, of

differents adsorbents, of different pretreatment schemes and of different source waters. Tests have been conducted in Cincinnati,OH; Manchester, NH; Jefferson Parish, LA; Evansville, IN; Miami, FL; Huntington, WV; Beaver Falls, PA; Passaic, NJ; Thornton, CO; Philadelphia, PA; Shrevenport, LA (Lykins and Adams (1984)). Evaluations of toxic organic removal have also been conducted at pilot scale and full scale facilities in France, Germany, Holland, Switzerland, Belgium and England (NATO (1984)).

These investigations yielded several important results. First, the results of each experiment are site specific, as the water matrix varies substantially with location. For example, background organics vary in concentration and in composition. Also the nature of the contamination varies; at Jefferson Parish, LA, 1,2-dichloroethane is constantly present in the raw water (Lykins and Adams (1984)) while at Cincinnati, OH, there are frequent spills (DeMarco et al (1983)) and at Shrevenport, LA, the water is virtually free of anthropogenic chemicals (Glaze et al (1983)).

Second, the background humic substances, which are the most prevalent group of organics in natural waters, are the first organics observed in the GAC column effluents. The background organics have a very characteristic breakthrough curve which includes continuous removal of 10 to 30 percent of the influent over a very long period of time (see Section 2.4.2 and Figure 2.3).

Third, in plants practicing pre-chlorination, trihalomethanes (THMs) are the next set of organic substances to appear in the column effluent. In water treatment plants, chloroform is the most common trihalomethane and it is the first to breakthrough. It is followed by

bromodichloroethane, dibromochloroethane and bromoform, which is the order of increasing adsorption capacity and they have relatively sharp breakthroughs (Figure 2.4). Due to their low adsorptivity and to competition with other more strongly adsorbed organics, such as the background organics, the THMs are often displaced. This displacement causes the effluent concentration to exceed that of the influent, i.e., an overshoot (Figures 2.4 and 2.5).

Fourth, the next compounds to appear in GAC effluents are the next weakest organic compounds within the water matrix. Often, they are the volatile halogenated compounds such as 1,2-dichloroethane and 1,1,1-trichloroethane. In cases where pre-chlorination is not utilized, such as in many groundwater treatment applications, these compounds are the first toxic organics to breakthrough. As shown by Figure 2.6, these organics also display concentration overshoots as a result of competition (Yohe (1982), Suffet et al (1985)). If the adsorbers are allowed to operate for a long period, more compounds would pass through the column. Their order of appearance in the effluent is dictated by the relative adsorptivity of these compounds within the competitive adsorption that takes place within the column, thus this order is affected by the relative concentrations of these compounds in the feed (Chrostowski et al (1983)).

Finally, the concentrations of the many contaminants in the source water constantly fluctuate, thus causing a continuous re-equilibration of the different adsorbed contaminants. This has frequently led to unexpected displacement of toxic organics into the effluent (Yohe (1982)). Therefore, it is evident that study of competitive adsorption and desorption are of great importance, as they

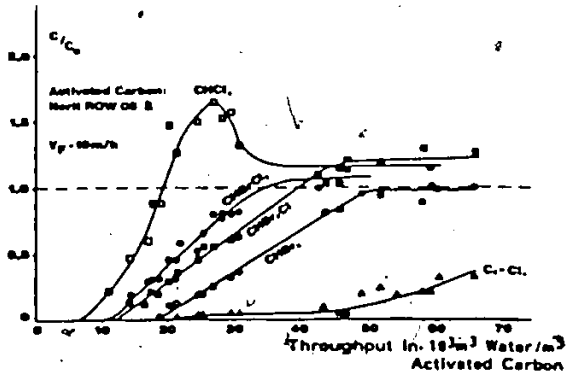

FIGURE 2.4 Breakthrough Curves of the THMs and Tetrachloroethylene at Hockirchen, West Germany. (after Fokken and Kurz (1984))

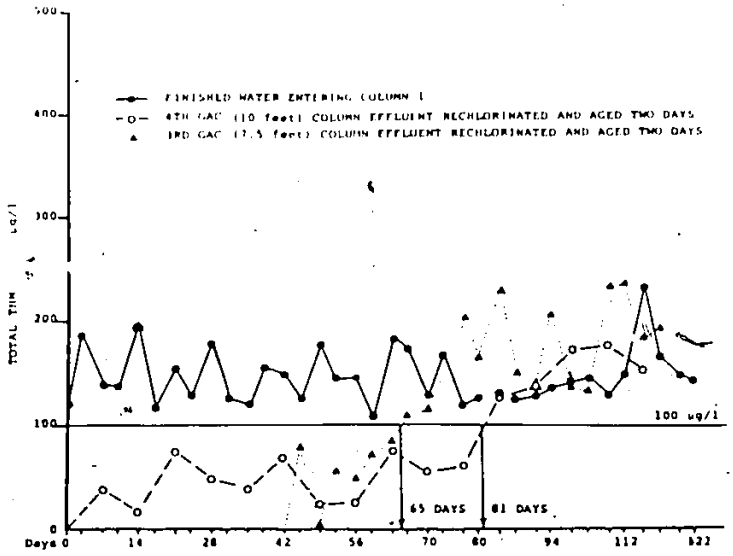

FIGURE 2.5 Total THM in GAC Column Effluents at Miami, FL. (after Woods and DeMarco (1980))

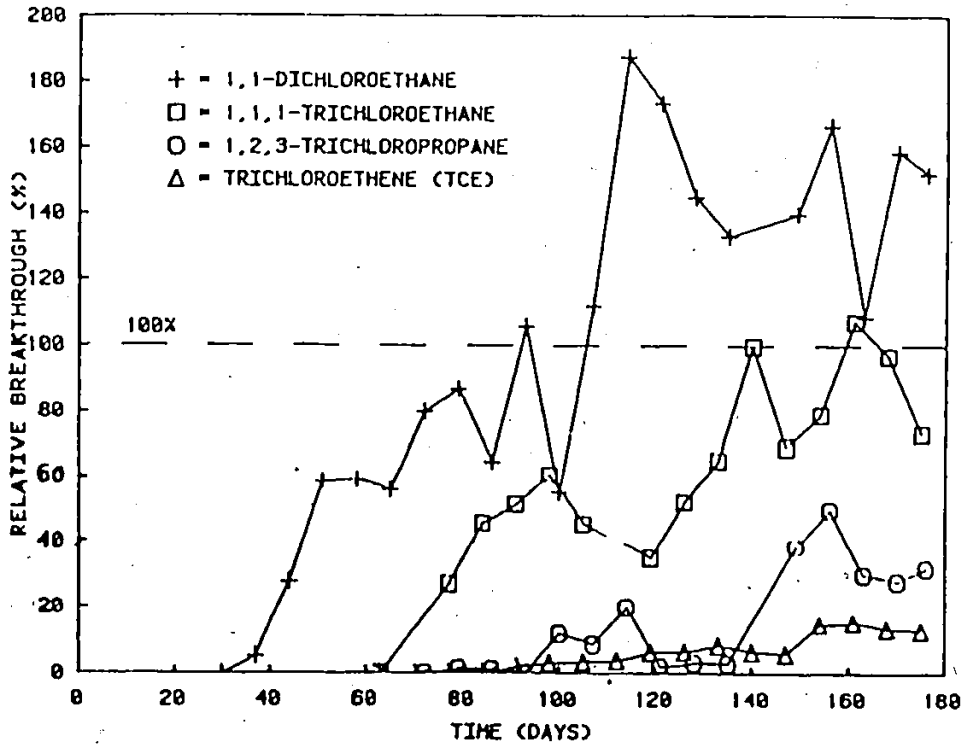

FIGURE 2.6 Relative Breakthrough Curves of Synthetic Organic Chemicals for Pilot Column #3, at the Groundwater Fed Upper Merion Reservoir, Philadelphia, PA. (after Yohe (1982))

are the key to the leaching of potential dangerous organics into drinking water supplies. As discussed in this chapter, these phenomena are not well understood. Thus, the objective of this dissertation is to investigate and model these phenomena in order to design and operate adsorbers that produce good quality water.

CHAPTER THREE

EXPERIMENTAL MATERIALS AND METHODS

3.1 ADSORBATES

This study used two adsorbates: 1,1,2-trichloroethane (TCEA) and naturally occurring organics. The TCEA was manufactured by Fluka AG (min. purity 99%). The natural occurring organics were part of a 300 L sample of the Groundhog River water collected in May 1982. This river is located in northern Ontario and the sampling point was near the town of Fauquier, thus this water will be called Fauquier river water (FRW).

Organic free water (OFW) was used for diluting the FRW, for preparing the TCEA solutions and standards, and for cleaning the glassware. The OFW was first distilled, then gravity fed at a rate of 2 to 3 liters/hr through an Ultrapure (mixed-bed) deionizing cartridge (Sybron Barnstead, Mass.) and a large GAC filter. This filter was packed with activated carbon from the same batch as that used in the experiments and it provided an empty bed contact time of approximately 9 hours. The TOC concentrations of OFW was always below 0.1 mg/ℓ.

The FRW, diluted FRW and the OFW were adjusted to a pH of 7.4 ± 0.1 using a 0.001 M phosphate buffer. These solutions required different proportions of analytical grade KH_2PO_4 and Na_2HPO_4 (BDH Chemicals, Toronto) to obtain this pH. The pH was monitored throughout the experimental program, and it was always in the range 7.3 to 7.6.

All the buffered solutions used in the adsorption experiments were filtered through 0.45 µm or 0.2 µm pore size cellulose nitrate membrane filters (Sartorius, West Germany), to reduce the possibility of bacterial growth. The filtration was carried out using a pressure filter propelled by a Masterflex peristaltic pump (Cole Palmer, Chicago, Ill.) so as to operate in a semi batch mode.

The TCEA solutions were prepared by spiking, with pure TCEA, buffered and filtered solutions in 20 or 45 ℓ carboys with very little freespace, and mixing overnight to obtain an uniform concentration.

3.2 ADSORBENT

The adsorbent used in all experiments was Filtrasorb F400 (Calgon Corp., Pittsburgh, Pa.). The activated carbon was sieved to obtain a 40X50 mesh GAC fraction and a PAC fraction with particles smaller than 200 mesh. Since the majority of the particles of F400 are in the 12X40 mesh range, the particles larger than 40 mesh were ground using a plate mill (Quaker City Mill, Philadelphia, Pa.), and resieved. Both the PAC and the GAC were boiled in OFW for 30 minutes, allowed to cool and settle, and rinsed with OFW to remove the fines. This procedure was then repeated. Then, the carbon was drained and dried at 105°C for several days. Finally, the carbon was cooled in a desicator and stored in well sealed glass jars.

3.3 ANALYTICAL TECHNIQUE

The TCEA was extracted with n-pentane which concentrated the TCEA by a factor of about 50. The extract was then analyzed with a HP-5880 gas chromatograph (Hewlett-Packard, Palo Alto, Ca.) with a Ni^{63} ECD detector. The chromatograph response was measured in terms of area

by a HP level IV integrator. Each sample was injected three times and the average peak area was used. A concentration versus area calibration curve was prepared for each analytical section using ten standards prepared in OFW and extracted by the same procedure as the samples. Detailed descriptions of the extraction procedure, gas chromatograph conditions, and Standard preparations are presented in Appendices A1, A2 and A3.

The background organics in FRW were measured in terms of total organic carbon (TOC). As in many studies reported in the literature, the UV absorbance of these humic solutions was linearly related to the TOC measurement (Figure 3.1). Although the UV-TOC correlation was used to reduce the number of TOC analyses, at least one third of the samples were analysed by TOC to provide the calibration curve. The TOC analysis was conducted using a Dorhman DC-54 Ultra Low Level TOC analyzer (Dorhman Instruments, Santa Clara, Ca.). According to the manufacturer, the measurements have a standard error of 0.01mg/ℓ for concentrations up to 0.5mg/ℓ and 2 percent at higher concentrations. In all mixed FRW - TCEA solutions, the reported TOC is that contributed by the background organics, as the contribution of the TCEA was subtracted.

The UV analyses were conducted with a Bausch and Lomb (Rochester, New York) Spectronic 21 UV-D variable wavelength spectrophotometer using 1 cm and 10 cm path length cells. The samples were analyzed at a wavelength of 254 nm, using an empty cell as reference, which was arbitrarily set at 0.100 absorbance units. Air was used as a reference as Benedek and Bancsi (1977) found it to be more consistent than distilled water. It should be noted that the TOC-UV relationship has a lower limit below which it is no longer linear. For

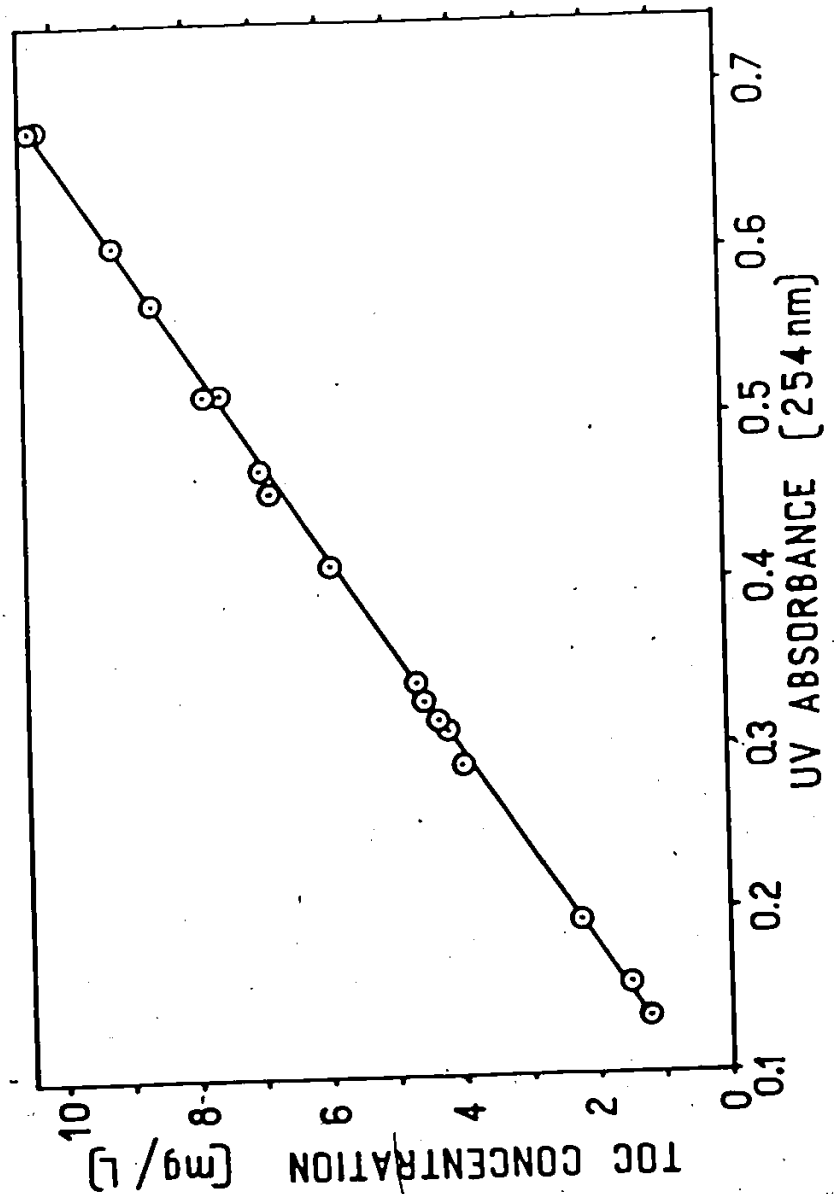

FIGURE 3.1 Typical Total Organic Carbon vs. UV Absorbance Curve.

the 1.0 cm cell path this limit was about 1 to 2 mg/ℓ, and for the 10 cm cell path it was about 0.15 to 0.25 mg/ℓ. If the absorbance is very low, i.e. the water is very clean (such as OFW), the relationship between UV and TOC is erratic. As a result, all the low level samples were analyzed by TOC.

3.4 EQUILIBRIUM STUDIES

The isotherms were conducted by the bottle point method outlined in section 2.2.1, using the same solution in all bottles and varying the carbon dosage. The solutions and the activated carbon were contacted in 500 ml glass bottles with teflon lined caps, so as to have inert vessels. The bottles were placed in an end-over-end tumbler which kept the particles in suspension and provided the necessary mixing. The tumbler was located in a constant temperature room operated at 20 ±1 °C. At the end of the contact period, the carbon was separated from the solution by pressure filtration through a 0.2 µm pore size membrane filter (Sartorius, West Germany). The filtrate was then analyzed as described in the previous section. A more detailed description of the isotherm experimental methods is presented in Appendix B1. Appendix B2 discusses the details of the filtration procedure.

PAC was used in the experiments to reduce the equilibrium time. Contact time was a minimum of 2 weeks, which was found to be satisfactory for the slower adsorbing background organics by Peel (1980), Lee and Snoeyink (1980), and Randtke and Snoeyink (1983). See section 2.2.1.1.

Several adsorption isotherms were conducted to describe a wide range of TCEA concentrations. Diluted FRW and FRW isotherms were conducted at different points in the experimental program, to account

for possible changes in the humics. As the intent of this thesis is to study water treatment adsorbers whose source water received a toxic spill, the TCEA concentrations used in the competitive isotherms, the batch kinetic tests and in the column run were significantly higher than those encountered during the normal operation of a water treatment plant. Three competitive adsorption isotherms were performed with initial concentrations listed in Table 3.1.

3.5 DESORPTION ISOTHERMS

The main difference between the adsorption and the desorption isotherms is the activated carbon used. The PAC used in each bottle of the desorption cycle originated from a different bottle in an adsorption isotherm. The loaded PAC was first transferred to the filter as part of the filtration step at the end of the adsorption cycle. The PAC was then immediately washed into a clean 500 ml glass bottle, filled with OFW and sealed. The bottles were then agitated in the end-over-end tumbler for a period lasting a minimum of a week longer than the adsorption cycle. Appendix B3 describes in detail the above steps.

3.6 BATCH KINETIC EXPERIMENTS

Batch kinetics tests measure the change in liquid phase concentration with time, arising from adsorption. The method used in this study was the same separate bottle for each data point approach used for obtaining the isotherms. The same GAC dosage was added to all of the bottles and they were contacted for different periods of time. The bottle-point procedure was slightly modified to improve the reproducibility of the carbon dosage measured (see Appendix B4).

These tests were carried out with GAC and the nominal initial

TABLE 3.1 Initial Concentrations in Multisolute Isotherms

COMPETITIVE ISOTHERM NO	INITIAL TOC CONC. (mg/ℓ)	INITIAL TCEA CONC. (mg/ℓ)
1	10.0	2.0
2	10.0	0.5
3	3.0	0.5

TABLE 3.2 Batch Kinetic Runs

RUN NO	INITIAL TOC CONC. (mg/ℓ)	INITIAL TCEA CONC. (mg/ℓ)	
I	5.0	---	background organics
II	---	0.5	1,1,2-Trichloroethane
III	5.0	0.5	mixed solution

concentrations for the three runs are presented in Table 3.2.

3.7 COLUMN RUN

This experiment used two 0.95 cm I.D. glass columns packed with known masses of 40X50 mesh media and operated in the downflow mode. A schematic of the system is presented in Figure 3.2. The columns were run in parallel, one was packed with sand and the second was packed with GAC with a 3 cm sand layer on top for flow distribution. The sand column was used as control to account for the possibility of biodegradation. The carbon was packed to a depth of 12.7 cm., providing an empty bed contact time of approximately 4.5 minutes and a hydraulic loading rate of 1.69 m/hr (0.67 gpm/ft^2).

The columns operation was divided into six stages, each with different feed concentrations (Table 3.3). The feed solutions with TCEA were prepared daily, and stored in an 8 liter refrigerated (5°C) reservoir to reduce possible volatization losses. The effluent lines passed through a small reservoir used for sample collection.

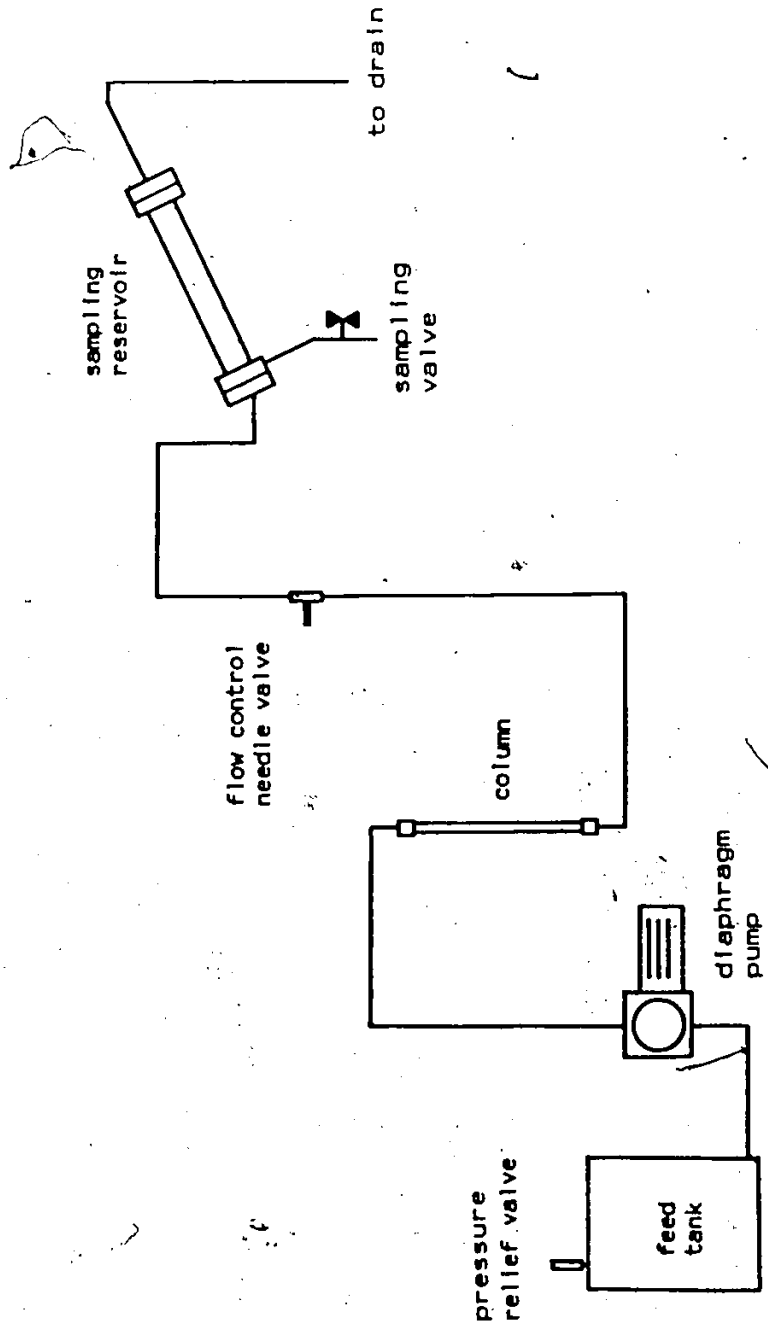

FIGURE 3.2 Schematic of Column Apparatus.

TABLE 3.3 Feed Concentrations of the Six Stages of the Column Run

STAGE NO	FEED BACKGROUND ORGANIC CONC. (mg TOC/ℓ)	FEED TCEA CONC. (mg TCEA/ℓ)
I	4.5	0.5
II	4.5	0.0
III	0.0	0.0
IV	9.0	0.0
V	0.0	0.0
VI	0.0	1.5

CHAPTER FOUR

EQUILIBRIUM STUDIES

4.1 SINGLE COMPONENT ISOTHERMS

4.1.1 1,1,2-Trichloroethane Adsorption

In order to cover a wide range of concentrations, several TCEA isotherms were conducted using solutions with different initial concentrations. Figure 4.1 shows the result of the experiments in terms of the logarithm of the solid phase concentration (q) versus the logarithm of the liquid phase concentration (c). (Data is tabulated in Appendix C1).

This data was regressed to fit Freundlich and Langmuir Model isotherm models using a nonlinear least squares routine. As explained by Sweeney *et al* (1982), regressing q versus c assumes that c is an independent variable, when in fact c is dependent on the carbon dosage, X. Thus these researchers suggested regressing c as a function of X, by utilizing the equation resulting from equating the isotherm model to the mass balance used to calculate q. This mass balance is

$$q = (c_0 - c) / X \qquad (4.1)$$

where c_0 = the initial liquid phase concentration, g/cm^3.

Thus for the Freundlich isotherm the following equation is regressed:

$$(c_0 - c) + X \cdot k \cdot c^n = 0 \qquad (4.2)$$

This nonlinear equation was solved using a variation of Newton's method

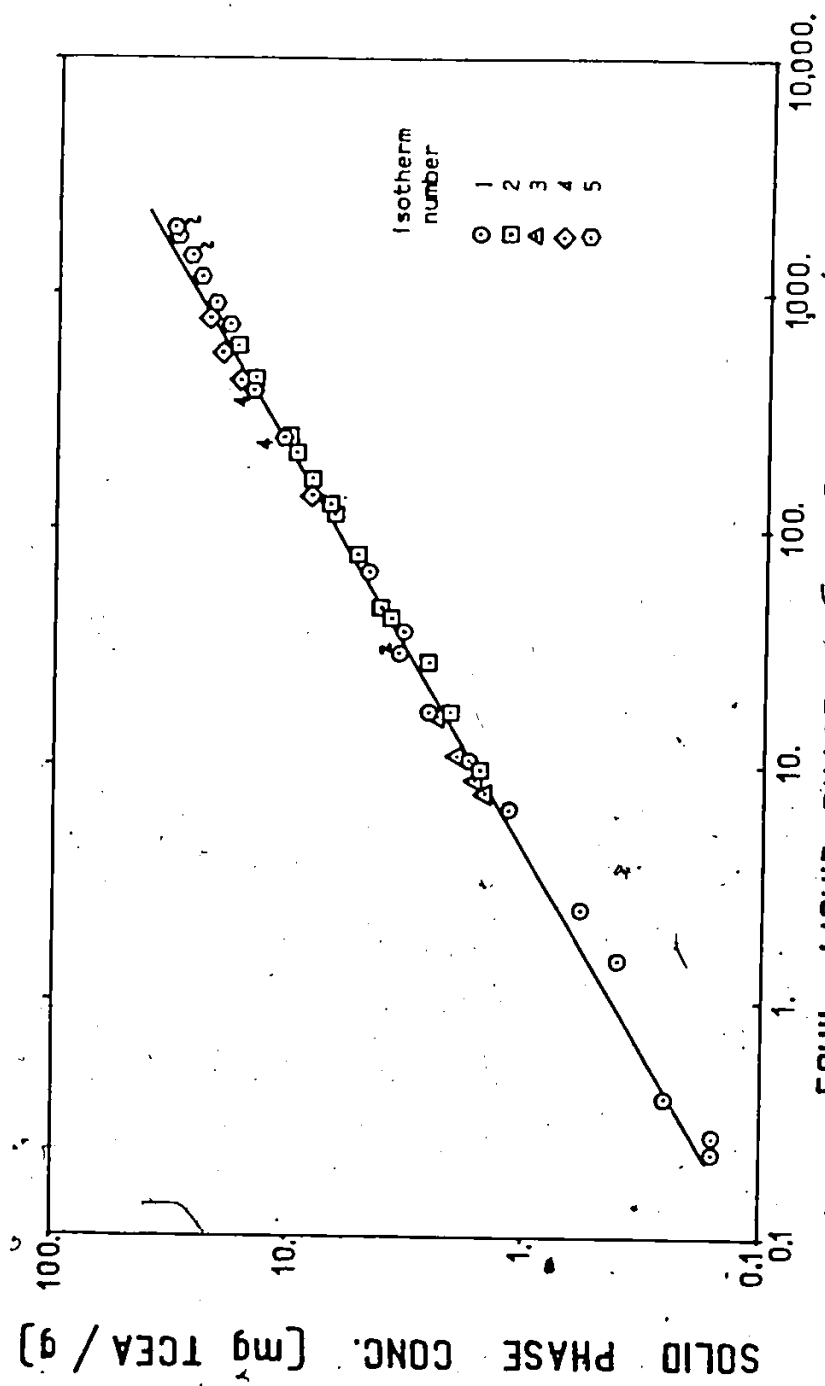

FIGURE 4.1 1,1,2-Trichloroethane Adsorption Isotherm.

which uses finite difference approximations to the Jacobian (Subroutine ZSPOW, IMSL (1982)).

The initial regression yielded a set of parameters which fit the higher valued data very well, but the lower valued data poorly. This was probably due to the data covering four orders of magnitude, and the predictions for the lower values had a smaller absolute error. To overcome this problem, the routine was modified to a weighted least squares, using the value of the observation. The objective function used was

$$\min \sum^{NP} (y/y - \hat{y}/y)^2 = \min \sum^{NP} (1 - \hat{y}/y)^2 \qquad (4.3)$$

where y = value of the observation;

$\hat{y}$ = value of the prediction; and,

NP= number of points.

This technique was used in conjunction with both the Freundlich and the Langmuir models. While the Langmuir model exhibited a poor fit over the entire span of the data, accurate fits could nevertheless be obtained within limited ranges. As anticipated from the straight line behaviour exhibited in Figure 4.1, the Freundlich model fit very well; the values of the regressed coefficients are shown below.

TABLE 4.1 Freundlich Isotherm Coefficients for TCEA

k	n
26.25 ± 5.3%	0.596 ± 2.4%

Dobbs and Cohen (1980) observed a 4.5 times smaller capacity for the adsorption of TCEA onto the same brand of carbon. Their results were obtained from isotherms with only a two hour contact period, thus the low adsorptivities were probably due to an insufficient contact

period to reach equilibrium.

4.1.2. Fauquier River Water Adsorption Isotherm

There are two important considerations in using natural water as the source of background organics. First, do the FRW and solutions of diluted FRW adsorb in the same manner? The results obtained in isotherm tests (Figure 4.2) indicate that they adsorb very similarly.

The second point of interest is: do the organics in the water remain the same with time? The TOC concentration of FRW dropped from approximately 12 mg/ℓ in July 1982 to about 9.5 mg/ℓ in November 1984, indicating that some changes occurred. Black and Christman (1963) and Gjessing (1976) observed similar changes. In addition, as shown in Figure 4.3 and Appendix C2, adsorption isotherms carried out on three occasions during the experimental program measured an increase in capacity with time. Based on the studies with different molecular weight fractions conducted by Lee and Snoeyink (1980), the increase in capacity can be attributed to a decrease in the average molecular weight of the humics. The actual mechanism of this change is open to question, but given the time span, even the slowest mechanisms, such as biodegradation, could have had an effect. Gjessing (1976) determined that only about 30 percent of the observed changes in TOC concentration could have been avoided by the use of 10 mg of $HgCl_2$ as a biocide. Black and Christman (1963) showed that losses in color could be significantly reduced but not completely eliminated by storing the water at a cold temperature under a nitrogen atmosphere. Such precautions were not possible in this case due to the lack of the proper facilities to store the 300 liter water sample. In recognition of this problem, the isotherms obtained near the time of the approximate experiments were

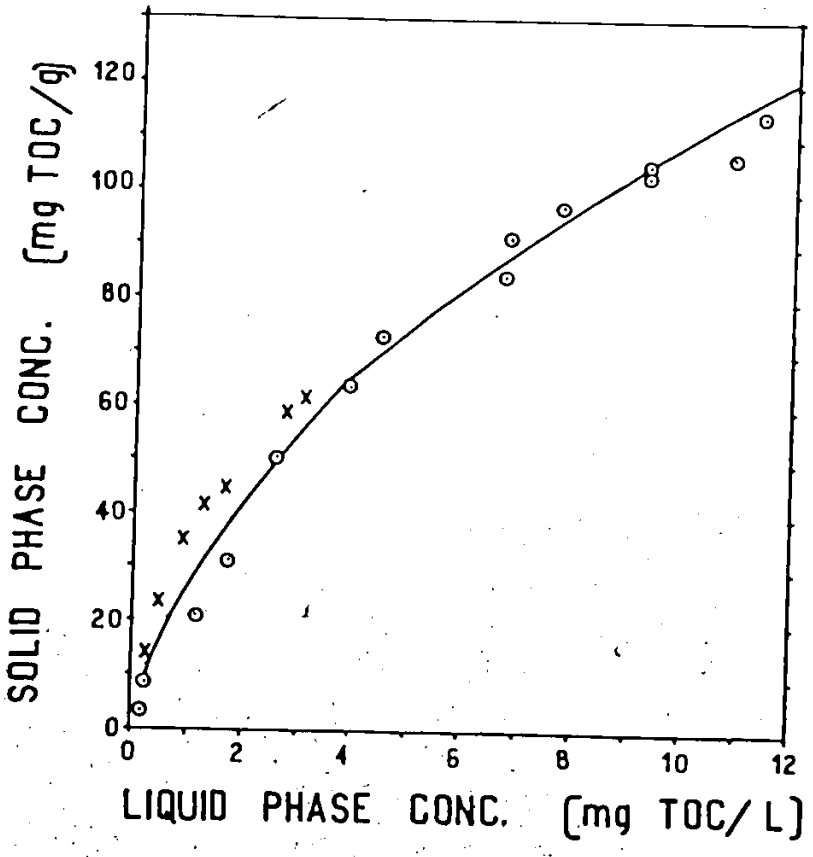

FIGURE 4.2 Fauquier River Water and Diluted Fauquier River Water Isotherms. (⊙ FRW; X Diluted FRW)

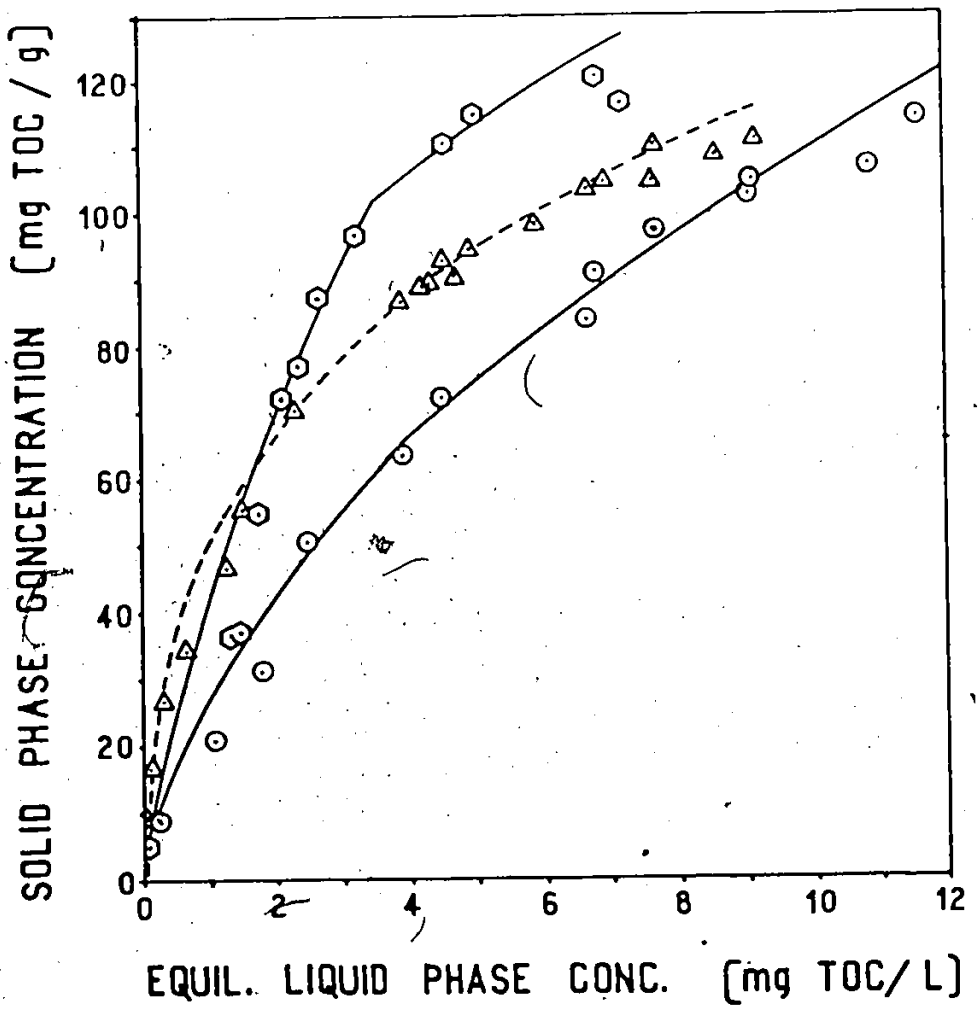

FIGURE 4.3 FRW Organics Isotherm at different points of this Study. (—⊙— 07/82; --△-- 10/83; —⊙— 11/84)

used in modeling the experimental data. As such, the second FRW isotherm was used for the modeling of the experiments conducted around the same time (i.e., the competitive isotherms and kinetics) and the final isotherm was used in the analysis of the column run.

Table 4.2 presents the results of the regressions of the three background organics using the nonlinear least squares method. As shown in this table, isotherms had to be split into two sections to allow description by Freundlich isotherms.

4.2 SINGLE COMPONENT DESORPTION EXPERIMENT

In theory, the desorption isotherm should either be the same as the adsorption isotherm, or higher. Identical adsorption and desorption isotherms represent completely reversible adsorption. The other extreme is completely irreversible adsorption. In this case the contaminant liquid phase and solid phase concentrations remain unchanged regardless of the initial liquid phase concentration of the desorption solution. Thus, the solid phase concentration is only a function of the loading attained during the adsorption cycle, and the desorption isotherms are horizontal or constant loading lines connecting the adsorption isotherm with the ordinate. When the desorption experiment consists of desorbing separately the carbon masses from the individual adsorption bottles, as the experiments undertaken in this thesis, it yields a set of horizontal desorption isotherms.

In the case of partially irreversible adsorption, the above experiments are similar to those of the fully irreversible case, in that they yield a set of desorption isotherms due to hysteresis effects. These isotherms also have higher loadings than the adsorption isotherm and they are slightly sloped. Figure 4.4 presents the phenol desorption

TABLE 4.2 Isotherm Parameters for Fauquier River Water

FAUQUIER ISOTHERM DATE	ISOTHERM CONC. RANGE	k	n	C_{non}
Aug. 1982	C < 3.6	27.1 ∓ 12.0%	0.653 ∓ 14.5%	0.00
	C > 3.6	30.8 ∓ 14.3%	0.551 ∓ 14.0%	
Oct. 1983	C < 4.08	50.95 ∓ 3.7%	0.401 ∓ 6.8%	0.054
	C > 4.08	56.52 ∓ 5.4%	0.3265 ∓ 10.0%	
Nov. 1984	C < 3.2	42.3 ∓ 11.6%	0.718 ∓ 16.5%	0.00
	C > 3.2	70.4 ∓ 14.3%	0.299 ∓ 31.3%	

LANGMUIR ISOTHERM DATE	ISOTHERM CONC. RANGE	QM	b	C_{non}
Oct. 1983	all	134.7 ∓ 4.7%	0.4737 ∓ 13.8%	0.00

- C_{non} = non-adsorbable concentration, mg TOC / ℓ

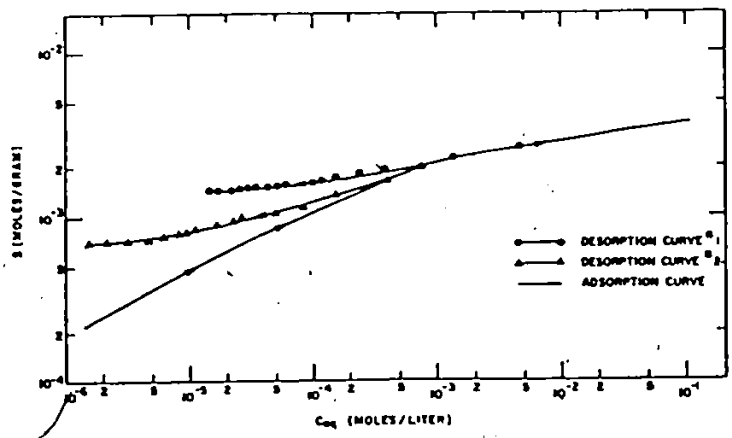

FIGURE 4.4 Adsorption and Desorption Isotherms of Phenol. (after Snoeylnk et al (1969))

isotherms for two masses of Columbia LC carbon obtained by Snoeyink et al (1969) which are good examples of partially irreversible adsorption. These desorption isotherms were obtained from multiple desorption cycles and the solid triangles and circles represent the conditions at the end of a cycle. The cycles were stopped when phenol no longer desorbed, thus the left end of the desorption isotherm is horizontal.

4.2.1 1,1,2-Trichloroethane Desorption Isotherm

Appendix C3 and Figure 4.5 show the data of two desorption isotherms which yield points slightly below those of the adsorption isotherm. However, error analysis (see appendices E1 & E2) showed that the 95% confidence interval of the adsorption and desorption isotherms overlapped, implying that observed differences were the result of experimental error. A third desorption isotherm was conducted to check if the buffering of the desorption distilled water was the cause of the observed behaviour. Two carbon dosages were used with OFW buffered in four different ways. The buffering only caused negligible differences, and these data are shown by the two solid squares in Figure 4.5. Thus the adsorption of TCEA is completely reversible.

The complete reversibility was expected as Weber and Pirbazari (1983) found carbon tetrachloride to be adsorbed reversibly onto the same brand of carbon as used in this study. Experiments with p-nitrophenol on BIO II GAC (Merk et al (1980)), and 3,5-dimethylphenol and 3,5-dichlorophenol respectively on 80317 and HD 3000 GAC (Thacker et al (1981)) have shown complete reversibility. Yet other cases of relatively small adsorbate molecules such as phenol and p-nitrophenol on Columbia LC carbon (Snoeyink et al (1969)) and p-nitrophenol on Nuchar

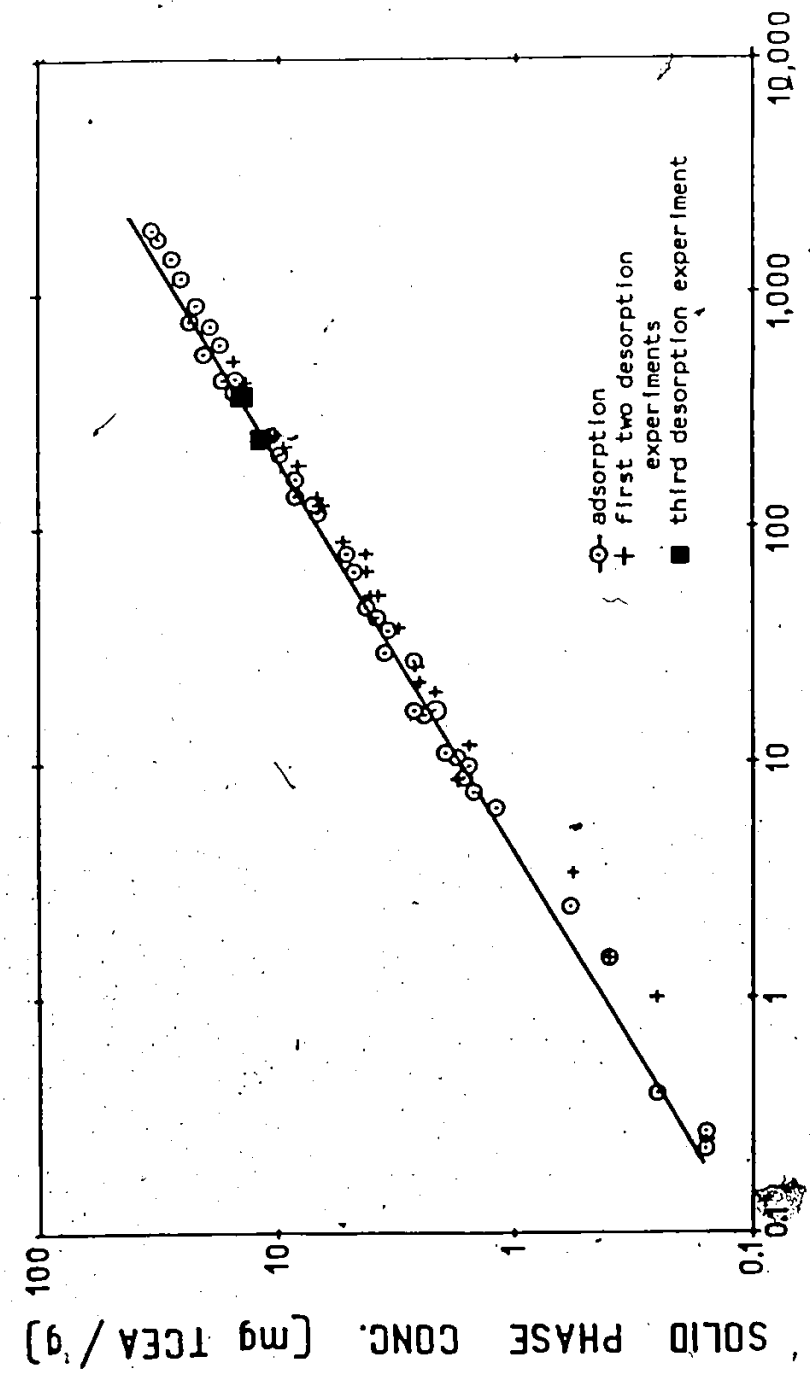

FIGURE 4.5 1,1,2-Trichloroethane Adsorption and Desorption Isotherms.

C-1000 (Mattson and Mark (1971)) indicate that there is some irreversibility. Therefore, the relatively little information available on the desorption of low molecular weight organics is inconclusive.

4.2.2 Fauquier River Water Desorption Isotherm

The desorption isotherm for FRW is shown in Figure 4.6 and listed in Appendix C4. The dashed line in this graph represents the results of the desorption isotherm, but as discussed in section 4.2, it is not the desorption isotherm. As the result of the hysteresis, this experiment yields a set of desorption isotherms, represented by lines connecting the equilibrium conditions before and after the desorption experiment (Figure 4.7). In order to obtain a complete isotherm several desorption cycles must be conducted. In this particular study, due to the limited extent of desorption of the background organics the equilibrium desorption concentrations are very low, and a second desorption cycle would have yielded little additional information.

The apparent irreversible adsorption of the FRW organics may actually be reversible, but then the desorption kinetics would have to be extremely slow. It should be noted that the contact period of the desorption cycle was one week longer than the adsorption cycle and that, as shown in section 5.3.2, the kinetics of adsorption are among the slowest reported to date for aqueous phase adsorption. Thus if the apparent irreversibility is a kinetics controlled phenomenon, the kinetics are so slow that for all practical applications of GAC adsorbers, the adsorption of FRW organics would be essentially irreversible.

The highly irreversible adsorption of FRW was expected as humics are known to be removed mainly by the slow adsorption mechanism, which

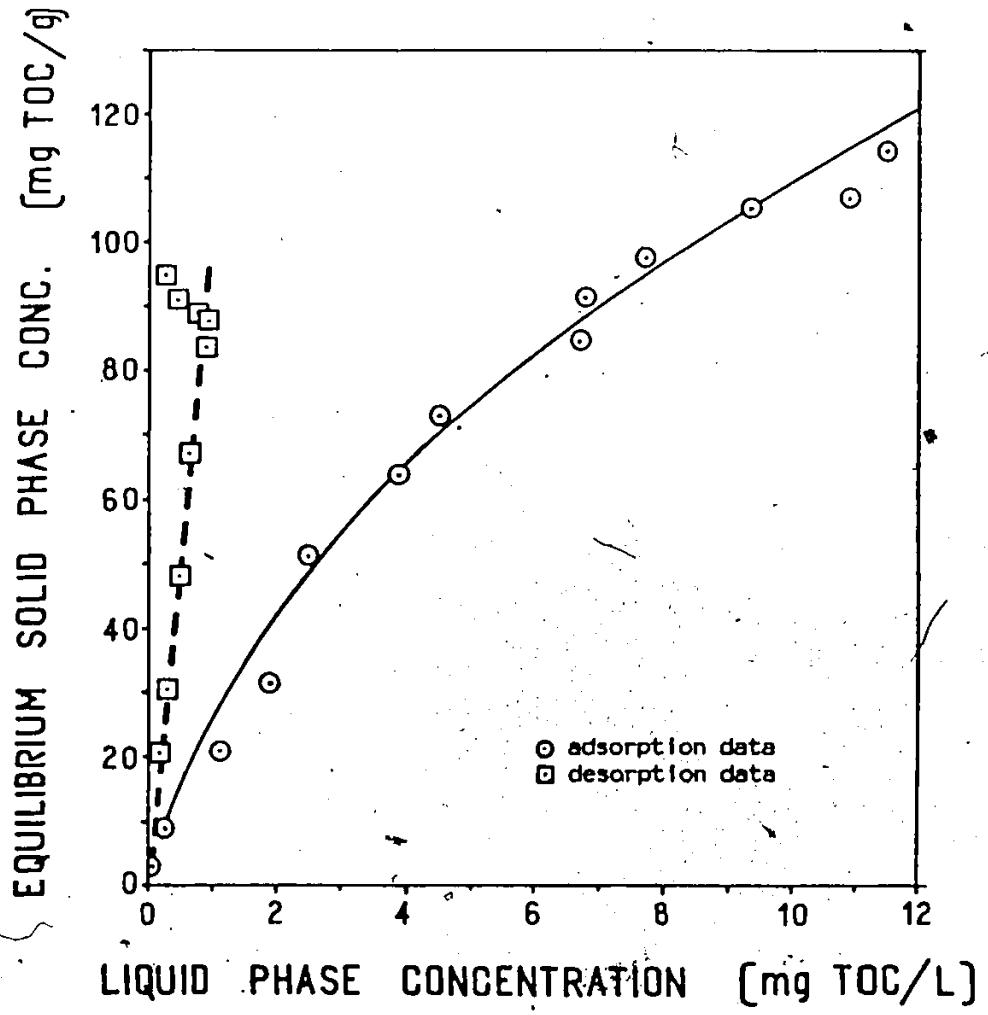

FIGURE 4.6 Fauquier Adsorption and Desorption Data.

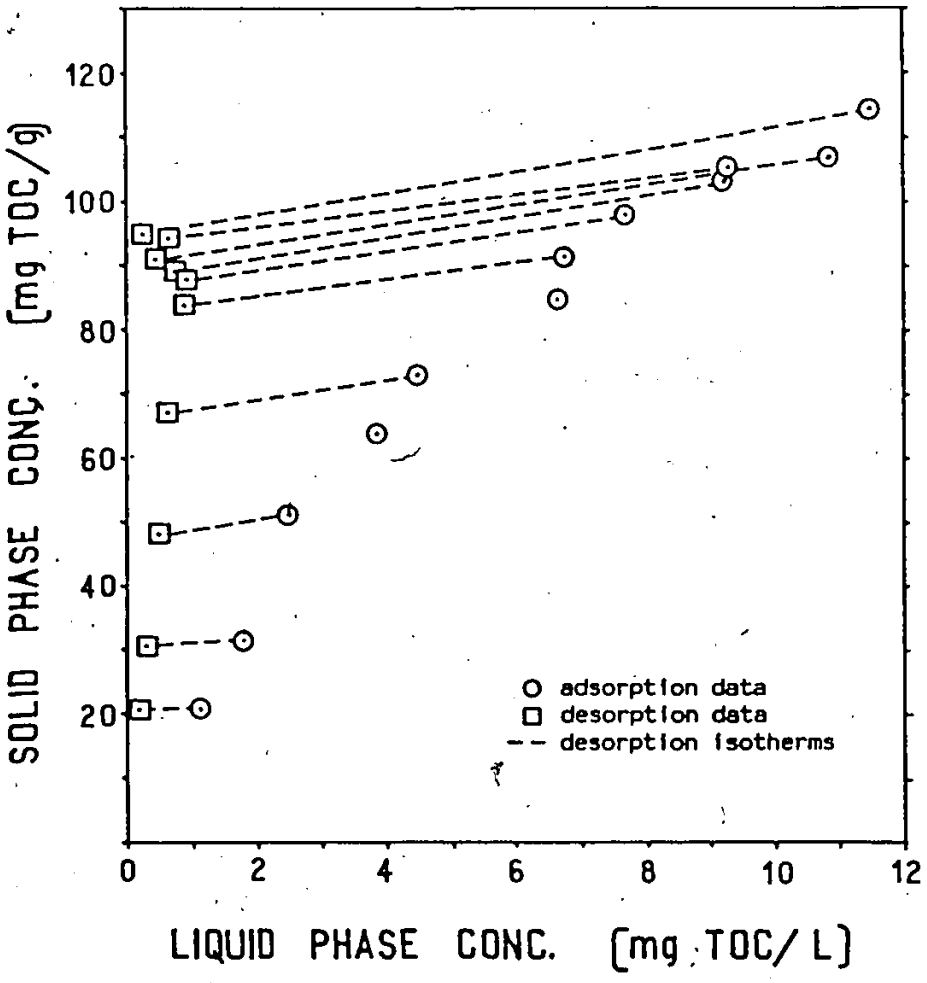

FIGURE 4.7 Fauquier Adsorption and Desorption Isotherms.

is hypothesized to be caused by steric hindrances or slow chemical reactions. And these same mechanisms are likely to cause irreversible adsorption. This is supported qualitatively by the research of Snoeyink et al (1969) on the adsorption and desorption of p-nitrophenol on Nuchar C-100. During the desorption cycles, they observed only a slight hysteresis effect when 20 minute adsorption and desorption cycles were performed (i.e., non equilibrium), and they observed substantial hysteresis when 10 day adsorption and 3 day desorption cycles were conducted. In the short adsorption cycles, the slow adsorption mechanism is expected to have a negligible effect and thus the above hypothesis would predict the small hysteresis effect observed. In the long contact experiments, the slow adsorption mechanism is expected to play an important role and thus significant irreversibility would be expected.

The high degree of irreversibility was also expected based on desorption data in the literature on other high molecular weight organics. Razzaghi (1976) had similar findings with Dextran T 70 (MW ≈ 70,000), bovine serum albumin (MW ≈ 69,000) and lignosulfonate (MW ≈ 60,000). Thus steric hindrances are a plausible explanation of the mechanism. Yet given sufficient time, these hindrances should not restrict desorption, and thus chemical reaction is a more likely explanation of the irreversible adsorption. The relationship between molecular weight and irreversible adsorption may be due to larger molecules being more reactive with the activated carbon surface. To evaluate the contribution of the two mechanisms more experimentation is required. Since chemisorption increases with temperature, adsorption - desorption tests at different temperatures may help distinguish between

the two proposed mechanisms.

The modeling of desorption isotherms is an area that has received limited attention. Di Toro and Horzempa (1982) developed two very simplistic models based on their tests of the adsorption and desorption of PCBs on clays and sediments. Although very useful, it is questionable whether these models can be applied to systems with non linear isotherms as some of the accompanying assumptions are clearly aided by the linearity of the data studied. In order to describe all of the data generated by desorption isotherms with a single equation, the following models will be tested. The first assumes that the desorption isotherm was a straight line, thus

$$q_{des} = q + a \cdot (c_{des} - c) \qquad (4.4)$$

where q_{des} = equilibrium solid phase concentration after the desorption cycle, g/g;

q = equilibrium solid phase concentration before the desorption cycle, g/g;

a = slope, cm^3/g;

c_{des} = equilibrium liquid phase concentration after the desorption cycle, g/cm^3; and,

c = equilibrium liquid phase concentration after the adsorption cycle, g/cm^3.

It was also assumed that the slope was an exponential function of q, in order to have a single equation to describe all the desorption isotherms. Thus

$$a = g1 \cdot q^{g2} \qquad (4.5)$$

where g1 and g2 are constants whose value is obtained by regression. As it can be seen on Figure 4.8, the desorption of the background organics

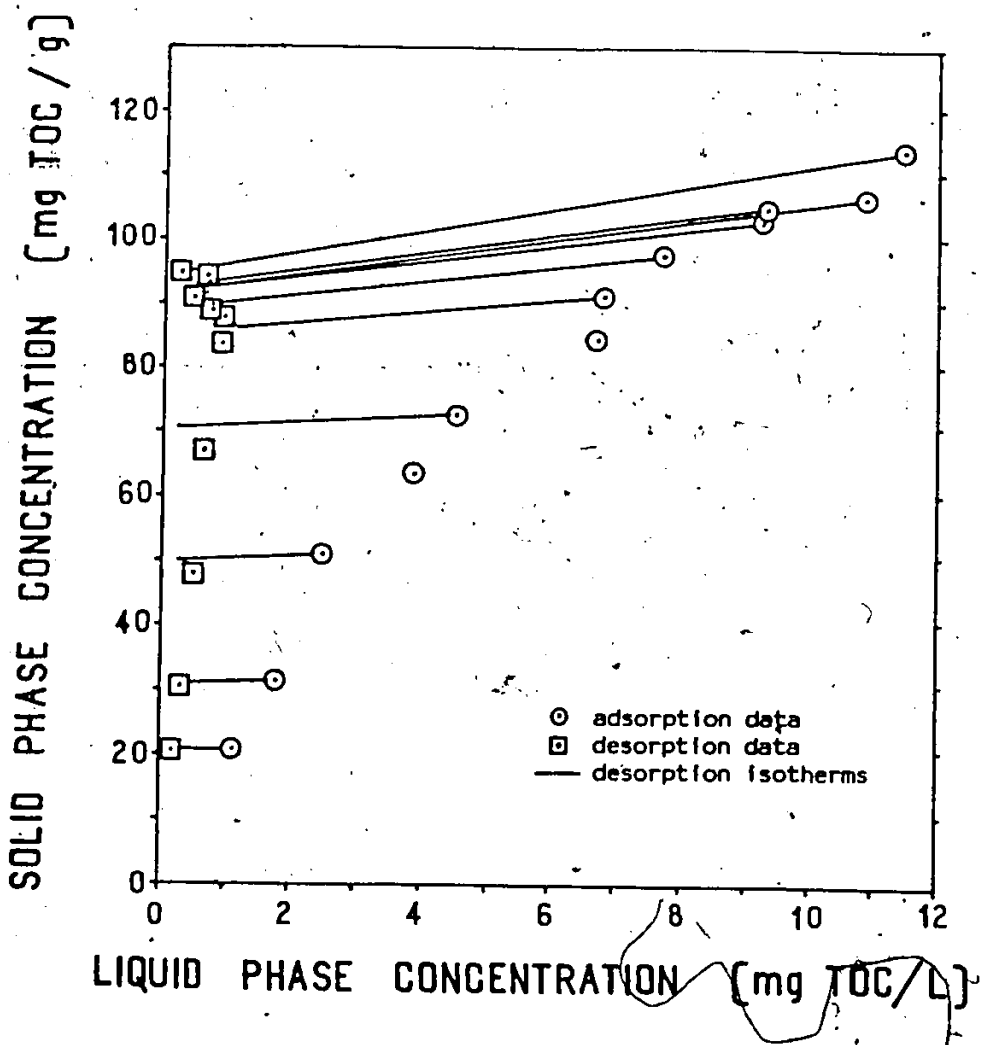

FIGURE 4.8 Regressed Desorption Isotherms of the Background Organics. (Equation (4.4))

can be described well by the above model.

The second model was intended for use in conjunction with the multicomponent modeling, so it was given the form of a Freundlich isotherm. This model is as follows:

$$q_{des} = g1 \cdot q^{g2} \cdot C_{des}^{(g3 \cdot q^{g4})} \qquad (4.6)$$

where g1, g2, g3 and g4 are constants. Table 4.3 presents the results of the regression of the FRW desorption data by equations 4.4 and 4.6. The results of the regression by equation 4.6 are presented in Figure 4.9. These models describe well the limited amount of data available, but more desorption data involving several desorption cycles is required to establish the suitability of these models.

4.3 BISOLUTE ADSORPTION EXPERIMENTS

As outlined in section 3.4, adsorption isotherms were conducted with three different mixtures of FRW and TCEA. In order to simulate the treatment of toxic spills, the bisolute equilibrium experiments utilized substantially higher TCEA concentrations than would be found under normal conditions at water treatment plants. Since there are two compounds present, each experiment yields one adsorption isotherm for each compound. The results of these experiments are presented in Appendix D1. Figure 4.10 shows the TCEA adsorption isotherm from isotherm M-1 and its repeat M-1B. The solid curve on top is the single solute TCEA isotherm. This figure indicates that there is a significant loss in adsorption capacity due to competition. As the liquid concentration increases, the loading first increases, then levels off, and finally appears to drop. Similar drops have been shown by Martin and Al-Bahrani (1977), Frick and Sontheimer (1983) and Crittenden et al (1984).

TABLE 4.3 Regression of the FRW Desorption Isotherms

	MODEL 4.4	MODEL 4.6
g1	0.1323	1.237
g2	0.5216	0.9349
g3	-	0.6843E-2
g4	-	0.4138
sum of squares	0.056197	0.106365

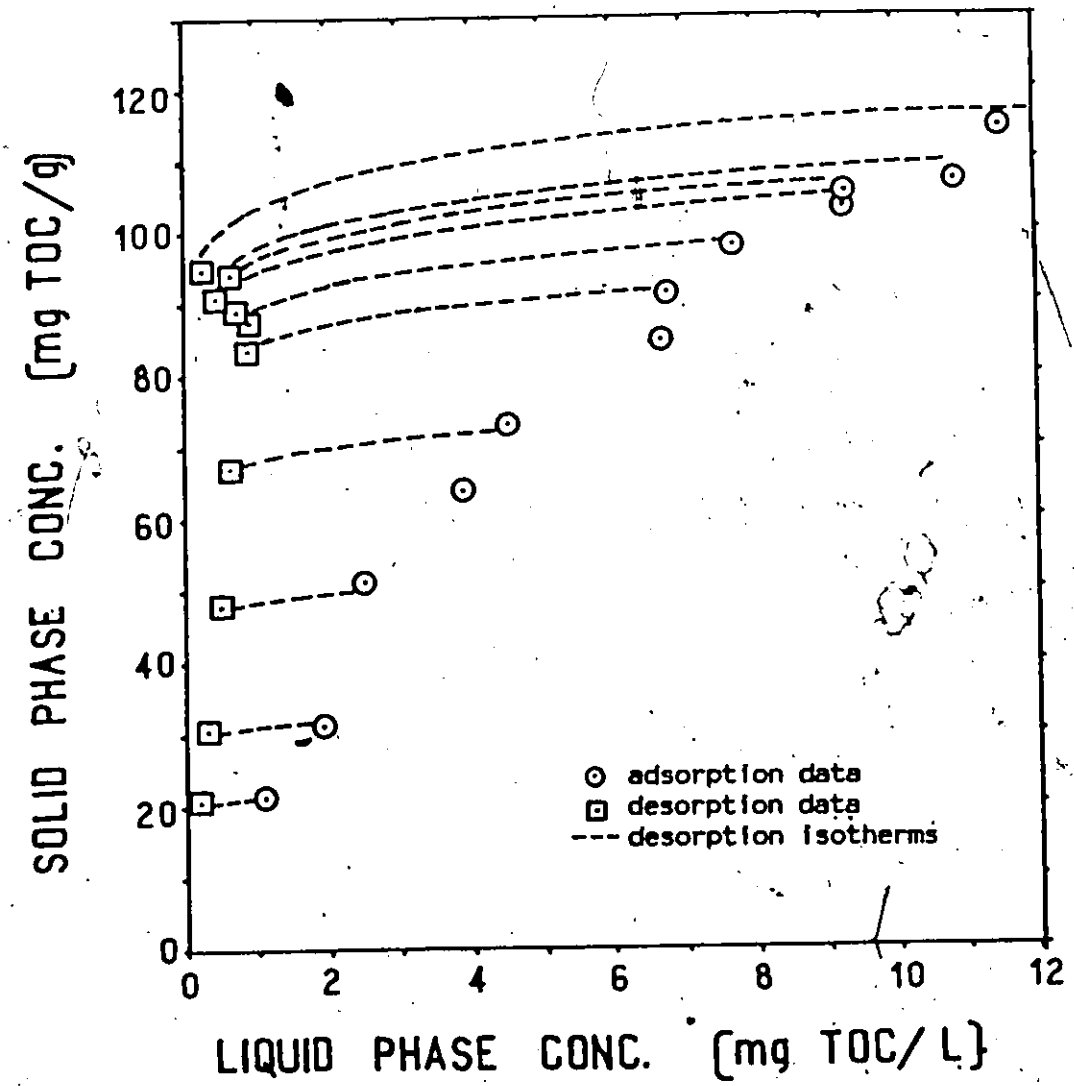

FIGURE 4.9 Regressed Desorption Isotherms of the Background Organics. (Equation (4.6))

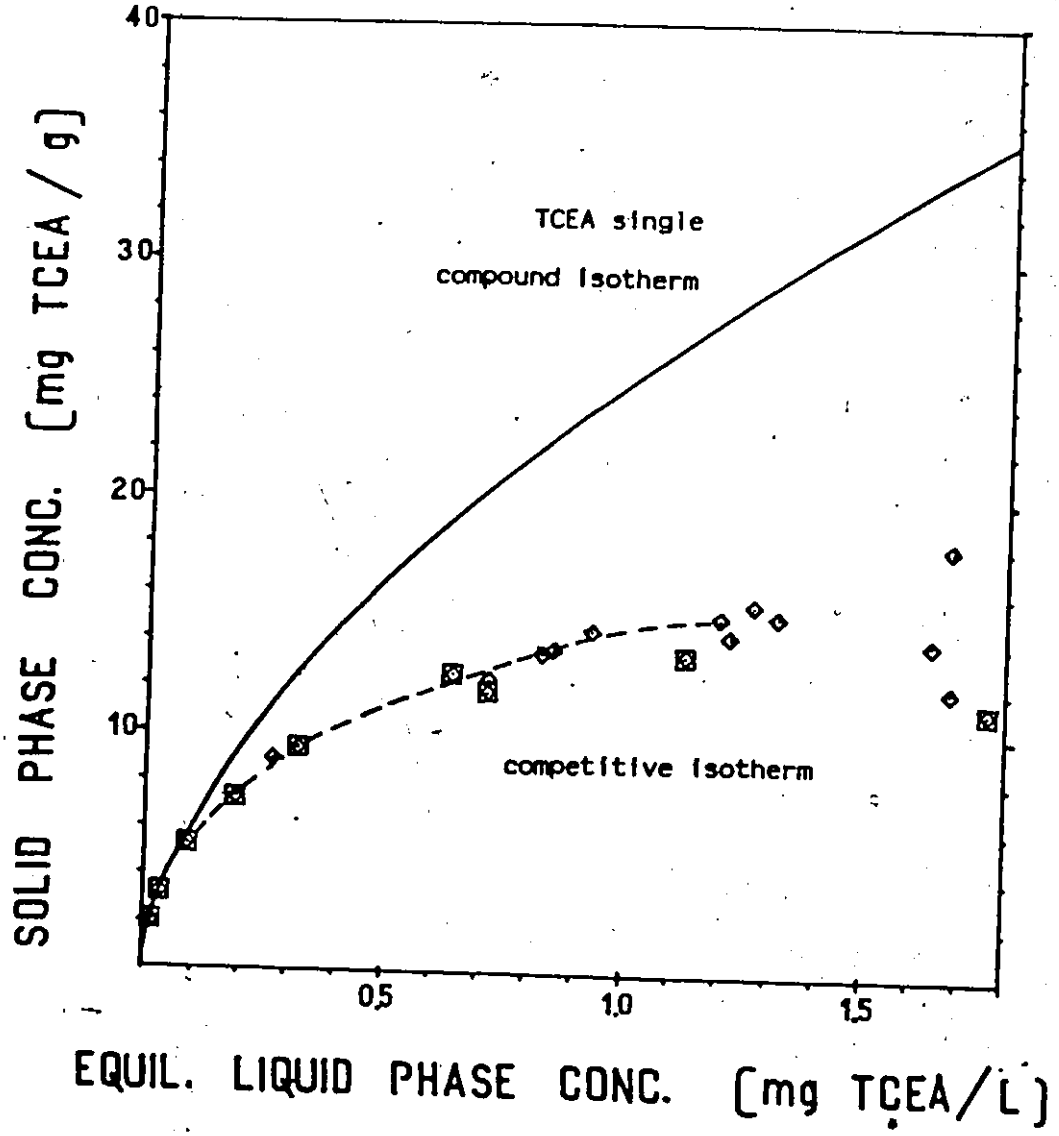

FIGURE 4.10 Competitive Isotherm #1 for Trichloroethane (TCEA).
[$C_{o_{TOC}}$ = 10.0 mg/L; $C_{o_{TCEA}}$ = 2050 µg/L;
◇ experiment #1;
⊡ repeat of experiment #1]

To assess the possible contribution of experimental error to the observed drop, the observations and their 95 percent confidence interval (see appendix E1) was plotted in Figure 4.11. From this graph it is obvious that due to the large error, the drop could be the result of experimental inaccuracies. The best way to study this phenomenon while reducing the experimental error would be to conduct isotherms with a microcolumn system like those proposed by Bilello and Beaudet (1983).

The other two TCEA competitive isotherms are shown in Figure 4.12, and show a similar pattern to that of the first experiment. The confidence intervals of these two experiments had the same pattern as those of the first competitive isotherm. The second experiment, shown as the triangles in Figure 4.12, had a somewhat squarish isotherm. This is probably the result of the 3.6 to 5 times higher ratio of TOC to TCEA in the initial concentrations. The two isotherms with similar initial TCEA concentrations and fairly different initial TOC concentrations show that decreasing the TOC initial concentration significantly increases the TCEA loading. Figure 4.13 shows a similar increase in capacity when the initial TCEA concentration is increased.

The competitive isotherms of the naturally occurring organics are shown in Figure 4.14, along with the single solute isotherm. The differences between these isotherms is minor, thus the presence of TCEA only slightly affects the FRW adsorption capacity.

The main results of these experiments are as follows. First, the adsorption of TCEA, the weaker adsorbing compound, was greatly affected by the initial concentrations of both compounds. Second, the adsorption of TCEA was greatly reduced by the presence of the natural organics, particularly as the equilibrium liquid phase concentration

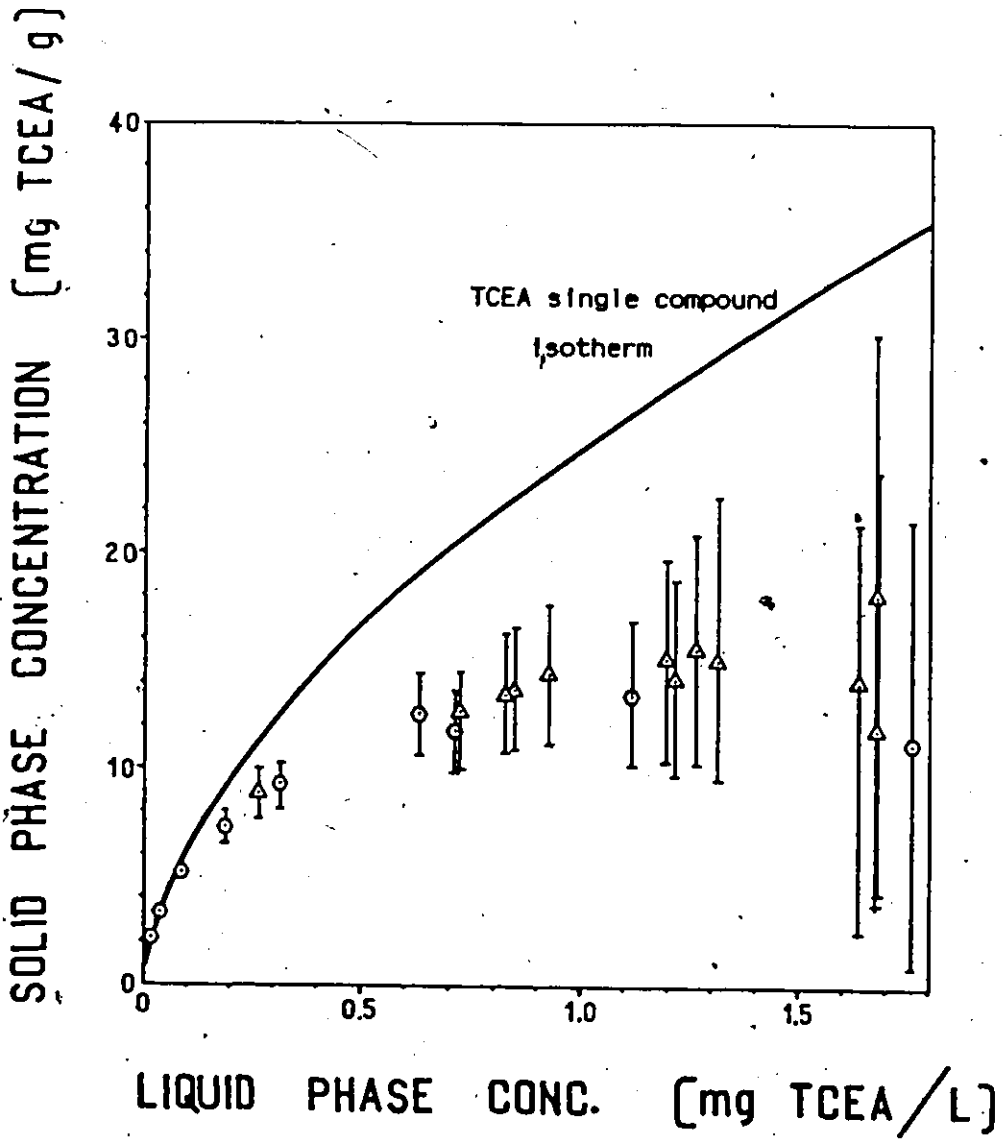

FIGURE 4.11 Competitive Isotherm #1 for Trichloroethane (TCEA) and their 95 Percent Confidence Interval Bars.

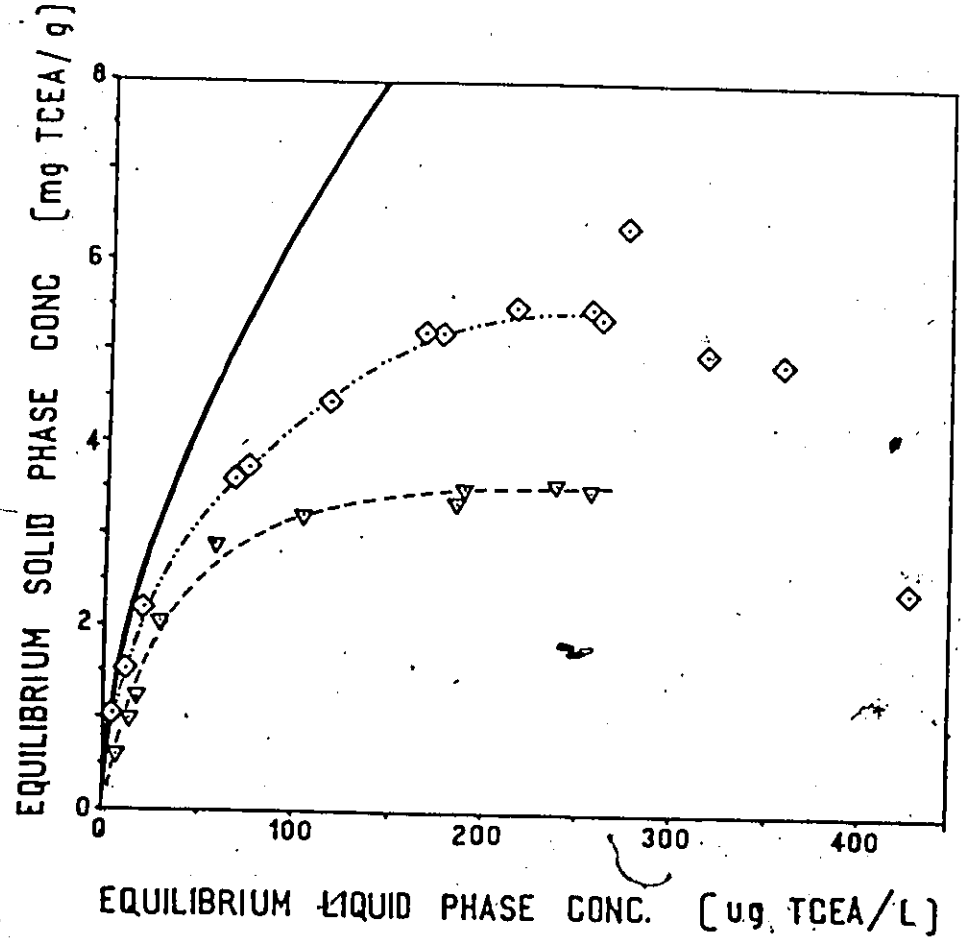

FIGURE 4.12 Competitive Isotherms #2 & #3 in Terms of TCEA.

	Init. TOC	Init. TCEA
competitive isotherm #2,	9.9 mg/ℓ	350 µg/ℓ
competitive isotherm #3,	3.5 mg/ℓ	450 µg/ℓ
single component.		

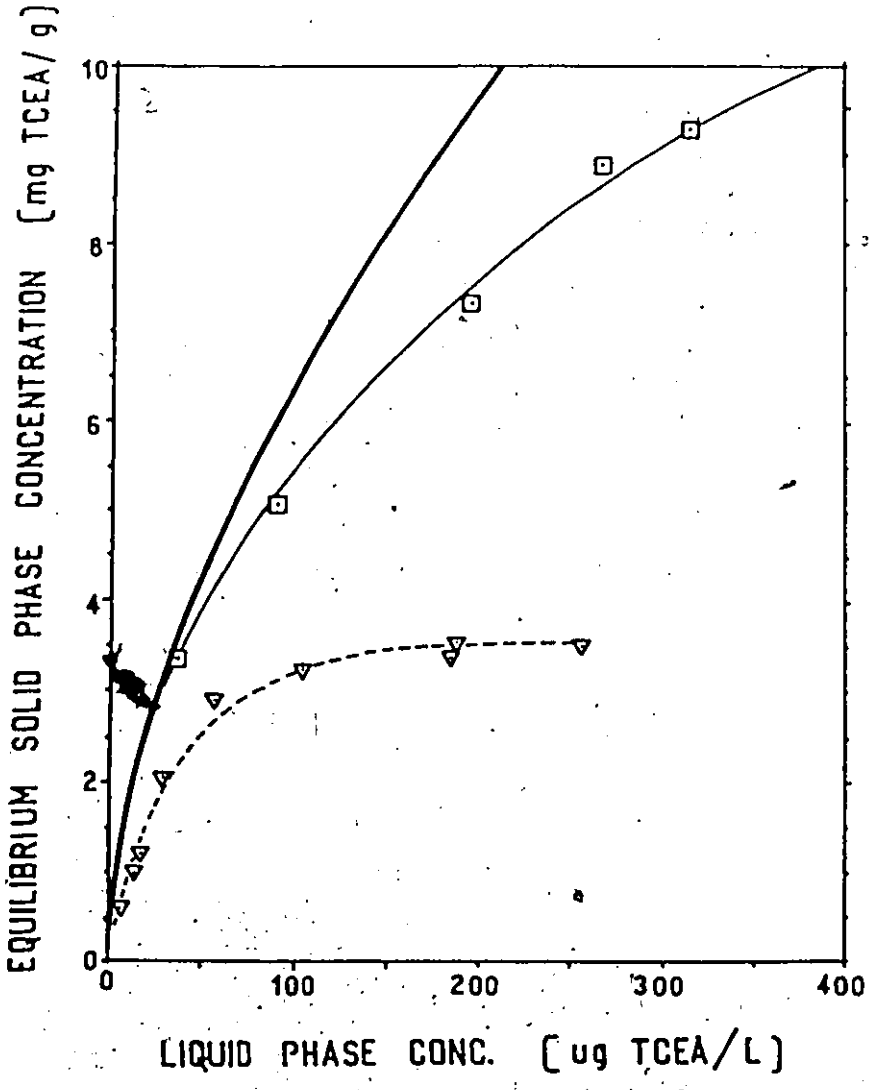

FIGURE 4.13 Effect of the Initial TCEA Concentration on the Competitive Isotherms.

	Init. TOC	Init. TCEA
competitive isotherm #1,	10.0 mg/ℓ	2050 µg/ℓ
competitive isotherm #2,	9.9 mg/ℓ	350 µg/ℓ
single component.		

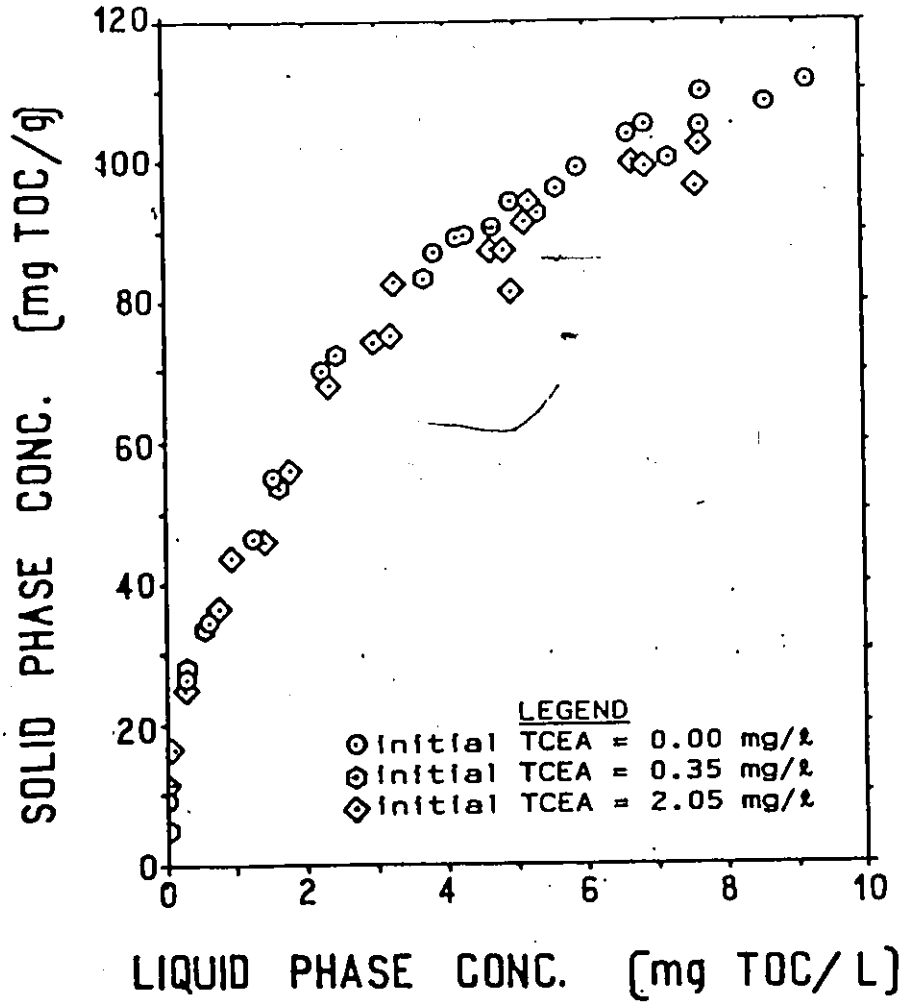

FIGURE 4.14 Fauquier River Water Isotherms.

approached the initial concentration. Third, on the other hand, the adsorption capacity of the FRW organics was almost unaffected. Since the background organics adsorb much better than the TCEA, probably some of these organics adsorb onto sites where there is no competition. This was somewhat expected as the compounds studied have very different molecular weights, and McCreary and Snoeyink (1980) discussed that this would be expected in such a situation.

4.4 BISOLUTE ISOTHERM MODELING WITH PREDICTIVE MODELS

This section will discuss the application of many of the models discussed in section 2.2.3 and of that described in the previous section, to the FRW organics - TCEA data. The majority of the competitive models are based on assumptions that require that all calculations be conducted on a molar basis. The background organics are composed of groups of molecules with widely different molecular weights. Although the molecular weight distribution of these organics could be measured, as discussed in section 2.3 there is significant controversy about the correctness of the different methods, since many yield widely different results for the same substance. Thus, it was assumed that the FRW organics had a constant molecular weight, expected to be in the range of the average molecular weight reported in the literature. As the actual organic carbon composition of the background organics is also unknown, the regressions of the competitive data will be used to determine the average TOC per mole of these organics. Based on reports in the literature, the molecular weight is expected to be approximately twice the TOC per mole ratio.

Since it was shown that the error for the points with higher equilibrium liquid phase concentrations was very large, it was decided

to limit the analysis to points with a maximum error of 25 percent (where the error is defined as the difference between the loading and its upper 95 percent confidence interval).

The initial evaluation of the models described in the literature was restricted to the predictive models. Simulations were conducted with different assumed molecular weights to detect the sensitivity of the models to this parameter.

The Jain and Snoeyink (1973) model was tested and found to yield some reasonable predictions at high values, but it was very poor at low values. This was mostly caused by the single solute Langmuir isotherms describing the data poorly over the lower region. Using two different Langmuir models over different regions to improve the simulations, created great discontinuities at the points where one model was substituted for the other, due to the sudden changes in the values of b. Due to these problems, this model was discarded.

The IAS model was found to predict fairly well the adsorption of the FRW organics, but to underestimate the TCEA adsorption capacity. Thus a model with a non-competitive term for the FRW organic model might improve the simulation of this data.

The SCAM model does not fit the data well; it underestimates the adsorption capacity of both components. The sensitivity analysis shows that the molecular weight of FRW organics should be significantly higher than 800 to improve the TCEA simulations and lower than 400 to improve the FRW organics simulations. Since it would therefore be impossible to improve the simulations of SCAM by adjusting the molecular weight, this model was also judged unsuitable for this application. The application of the modified SCAM model, described in the previous section, is

discussed below.

The Yonge and Keinath (1984) model was not tested since it would have yielded poorer predictions than SCAM. This is because it is a modification of SCAM that yields solid phase loading equal to or lower than SCAM.

The self calibration method described by Razzaghi (1976) for her model was tried but found to be unworkable for the data investigated. However, as this model contains non-competitive terms it has a good potential for describing the data, and thus it will be considered with the other regression based models.

Thus the predictive models presently available could not predict the data obtained in this study. The most likely reason is that there are adsorption sites where there is no competition, a possibility not allowed for by most the models tested. As a result, the regression-based models considered in section 4.6 include this feature, i.e., the Razzaghi (1976) model, and a new model proposed in the following section.

4.5 PROPOSED COMPETITIVE ISOTHERM MODEL

This model is based on the premise that not all of the adsorption sites are available for competition, and that adsorption on the competitive sites can be described by the SCAM model (see Section 2.2.3.1). It further assumes that the single solute component isotherms can be described by Freundlich isotherms, and the fraction of the adsorption capacities involved in competition are constant, regardless of the concentration. Thus the model is

$$q_i = (1-w_i)\cdot k_i \cdot c^{n_i} + KT\cdot(w_i\cdot k_i\cdot c_i^{n_i})^{1/n'} \cdot \left(\left(\sum_{j=1}^{NC} (w_j k_j/K')\cdot c_j^{n_j}\right)^{1/n'}\right)^{(n'-1)} \quad (4.7)$$

where $KT = K'^{((n'-1)/n')}$;

$$K' = \left(\prod_{j=1}^{NC} (w_j \cdot k_j) \right)^{(1/NC)} ;$$

$$n' = (1/NC) \cdot \sum_{j=1}^{NC} n_j ;$$

i = component index ;

NC = total number of components; and,

w_i = fraction of the adsorption capacity of solute i which occurs at sites where competition will occur.

The first term of the right hand side of equation 4.7 represents the non-competitive adsorption. The second term represents the competitive adsorption and it is the same as the SCAM model except that it uses the fraction of the adsorption of each compound involved in competition. This is achieved by replacing the Freundlich isotherm coefficients, k_i, by $w_i \cdot k_i$. Due to the general form of this model (equation 4.7) it can be used to describe systems with any number of solutes.

Because the value of the competitive fractions can only be obtained from competitive experiments, this is a regression based model. This model will be called modified SCAM (MSCAM).

4.6 BISOLUTE ISOTHERM MODELING WITH REGRESSION BASED MODELS

The regression based models tested in this section are the Razzaghi (1976) model and the MSCAM model (section 4.5). These models were chosen because they contain non-competitive terms, and the modeling of the data obtained in this study appeared to require such terms (section 4.4).

The regressed parameters for both these models were the fraction of the adsorptive capacity of component 1 involved in competitive adsorption (w_1), the analogous term for component 2 (w_2) and the average TOC per mole of background organics MW1. The background organics are

considered as component 1. The subroutine has no restriction on the values generated for the regressed parameters (BETA(1), BETA(2) and BETA(3)) other than the machine limits. Since w_1 and w_2 can only have values between 0 and 1, the program utilizes the following relationships

$$w_1 = 1. / (1+ABS(BETA(3)) \quad (4.8)$$

$$w_2 = 1. / (1+ABS(BETA(2)) \quad (4.9)$$

$$MW1 = BETA(1) \quad (4.10)$$

in order to ensure that w_1 and w_2 have feasible values. Due to the nature of the MSCAM and the Razzaghi models, MW1, BETA(2) and BETA(3) are expected to be highly correlated and the confidence intervals of the parameters will be very wide.

The Razzaghi and MSCAM models were calibrated using the programs RAZZ10 and MSIAS, respectively, which are listed in Appendices H1 and H2. The two non linear equations representing these models were solved simultaneously using the IMSL (1982) routine ZSPOW based on Newton's method with finite difference approximations for the Jacobian. The regression was carried out using the parameter estimation routine developed by Jutan (1976) for multiresponse data. This program is based on the Bayesian approach, which can be used to derive the least squares parameter estimation method for the single response case. This algorithm uses the Wilson (1970) approach and it actually minimizes the determinant of the variance covariance matrix of the residuals, D.

Regressions were conducted of the three competitive isotherms with different initial concentrations, both individually and combined. The results of these calculations are shown in Table 4.4, which yields two general characteristics. First, comparing the fits of both models

TABLE 4.4 Results of the Regression of the Competitive Isotherms

MODEL	EXPER-IMENT	MW1 EST.	σ	BETA(2) EST.	σ	BETA(3) EST.	σ	D	SS
RAZZAGHI	M1&M1B	317	494	-0.394	0.764	1.580	2.82	0.2586E-8	
	M2	1327	3451	-0.137	0.876	-1.40	5.81	0.4121E-9	
	M3	457	265	0.370	0.285	3.93	2.47	0.1787E-11	
	ALL	176	61.8	0.305	0.159	.602	.506	0.9934E-9	0.484
MSCAM	ALL	76.8	15.5	0.542	0.335	5.22	1.85	0.12614E-8	0.447
	M3	69.7	22.2	0.22E-6	7.84	13.8	90.7	0.6918E-11	
	M2	75.7	543	0.529	2.57	5.13	12.95	0.444E-9	
	M1&M1B	76.7	145	0.446	6.53	5.63	32.4	0.4330E-8	

- Actually regressed MW1 = TOC/mole,
  BETA(2) = $(1./w_2)-1$, and
  BETA(3) = $(1./w_1)-1$.

- D = variance covariance matrix of the residuals

- SS = sum of squares

for all the data, the Razzaghi model yields a slightly smaller determinant D than the MSCAM, but a slighly higher sum of squares. This indicates that both models fit the data equally well. The plotted results, such as Figures 4.15 and 4.16, give a similar appraisal. Second, comparison of the parameter values obtained by analyzing the individual experiments with the parameters of the combined data, showed that the MSCAM model has fairly consistent values while the Razzaghi model does not. For this reason the MSCAM model was chosen for the analysis of later adsorption experiments. One small drawback of this model is that it does not yield a smooth curve when the Freundlich isotherm of the background organics is changed from one section to the next.

Due to the uncertainty of the estimated parameters from both models, the interpretation of these results should be conducted with caution. Both models show that approximately 60 percent of the TCEA is adsorbed competitively. The regressions with the Razzaghi model estimate that about 60 percent of the background organics are involved in competitive adsorption while the regressions using the MSCAM model assess this fraction as 16 percent. Despite these differences, both models which contained non-competitive terms described the data well, while others which did not use such terms were not as successful. Thus it is likely that some sites can adsorb only TCEA or FRW, and other sites can adsorb both, with competitive adsorption occurring only at the second type of site.

The Razzaghi model estimates that the average molecular weight of the organics is approximately 350, while the estimate of the other model is half of this value. Both these values are low when compared to

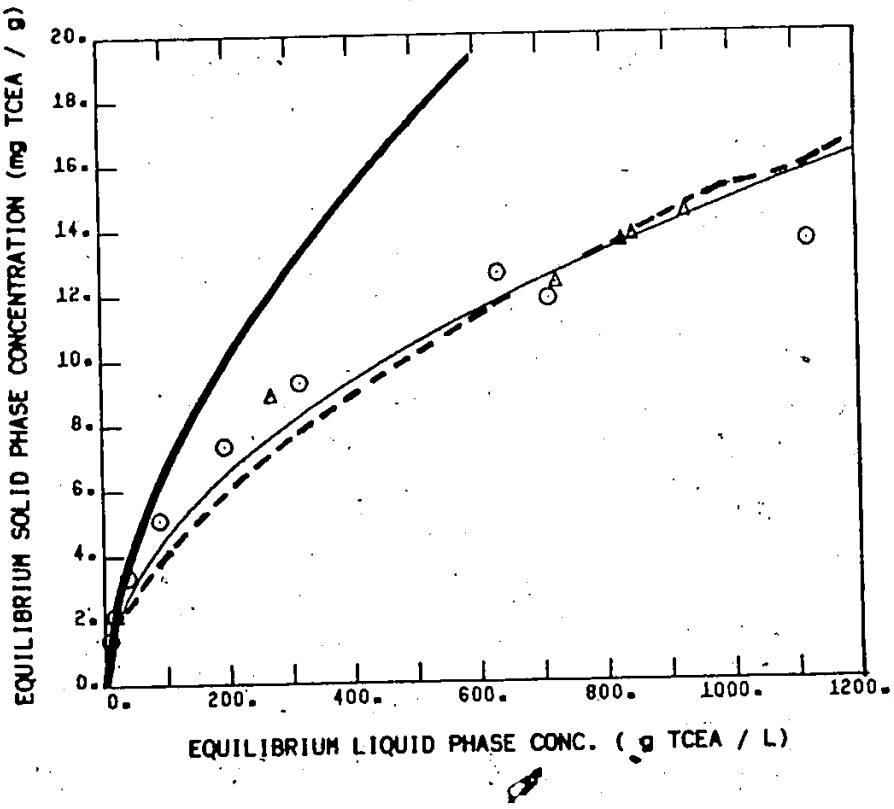

FIGURE 4.15 Simulations of TCEA Adsorption in Competitive Isotherm #1. (⊙ experiment #1; ▲ repeat of experiment #1; - - - - Razzaghi model simulation; ——— MSCAM simulation; and, ▬▬▬ single component isotherm.)

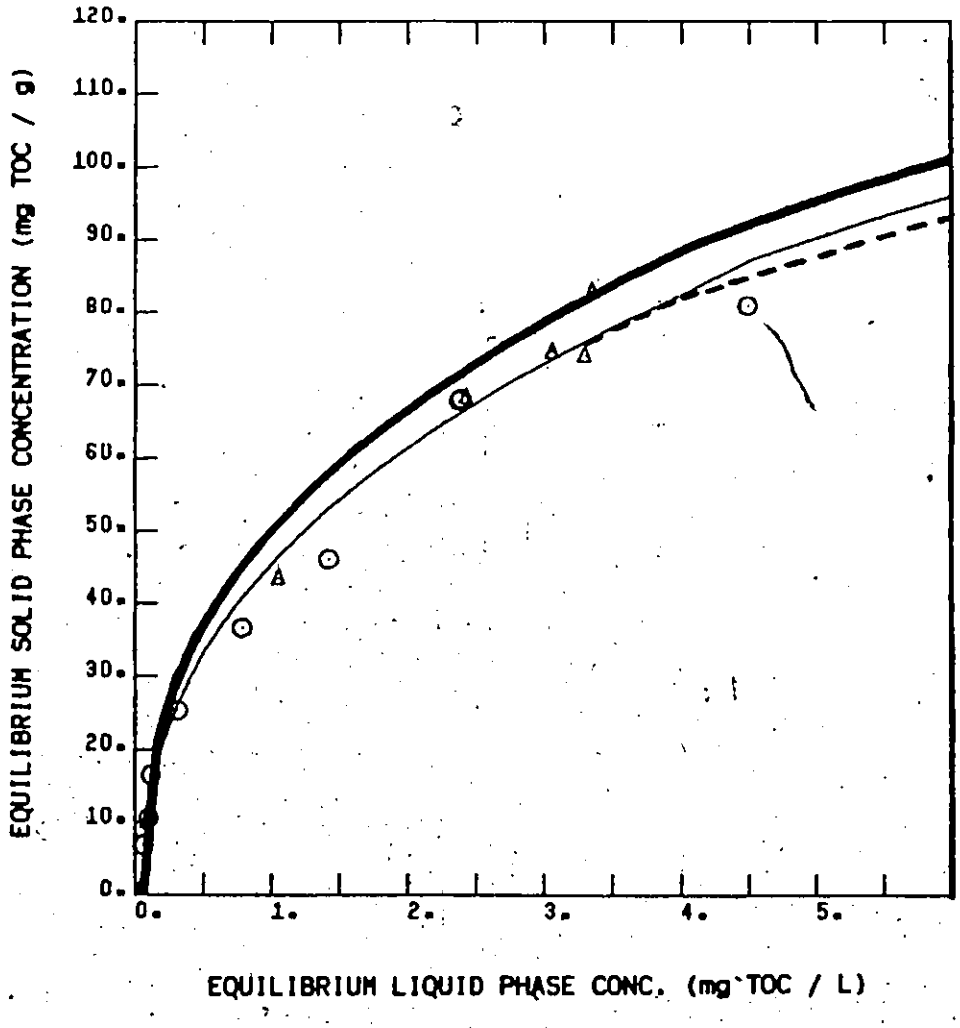

FIGURE 4.16 Simulations of FRW Adsorption in Competitive Isotherm #1. (⊙ experiment #1; Δ repeat of experiment #1; — — — Razzaghi model simulation; ——— MSCAM simulation; and, ▬▬ single component isotherm.)

those in Table 2.1, and this is possibly caused by the fact that the models tested are too simplistic to describe the complex process being studied. However, this could also be the result of the lower molecular fraction controlling the adsorption of all the background organics. McCreary and Snoeyink (1980) found the isotherm of the unfractionated solution of soil fulvic acid to be similar to that of the smallest molecular weight fraction, despite the fact that this fraction composed only 23 percent of the organics. This result is surprising since the general trend is that increases in the molecular weight result in decreases in the solubility and increases in the adsorption capacities. The uncharacteristic results observed by McCreary and Snoeyink (1980) may originate from differences in the behaviour of soil and aquatic humics. For example the adsorption capacity of the soil fulvic acids used by the above researchers was about one order of magnitude smaller than that of the FRW.

CHAPTER FIVE

BATCH KINETIC EXPERIMENTS

5.1 SINGLE COMPONENT ADSORPTION KINETIC MODELING

The dual rate kinetic model based on the homogeneous solid surface diffusion developed by Peel (1980) will be used to simulate the results of the kinetic studies. It was chosen because it has been shown to describe adsorption of a variety of different organics, including treated lake water, and the FRW organics are expected to behave similarly. As discussed in section 2.4.2, researchers using the conventional surface diffusion model were not as successful in modeling humic substances. In any case, by changing the values of two parameters, this model reduces to the homogeneous solid surface diffusion so that it can easily be used for comparisons.

As explained in section 2.2.4, Peel observed that adsorption occurred in two widely different rates. The rapid adsorption was attributed to unhindered mass transfer occurring in the larger pores. The slower adsorption was suspected to occur in the remaining pores, with radii of comparable size to the adsorbing molecule, thus hindering the mass transfer rates. These two types of pores have been called macropores and micropores, however these names are unrelated to the conventional definitions given to these terms. Figure 5.1 presents a schematic of the proposed model. The mass transfer involves 1) liquid

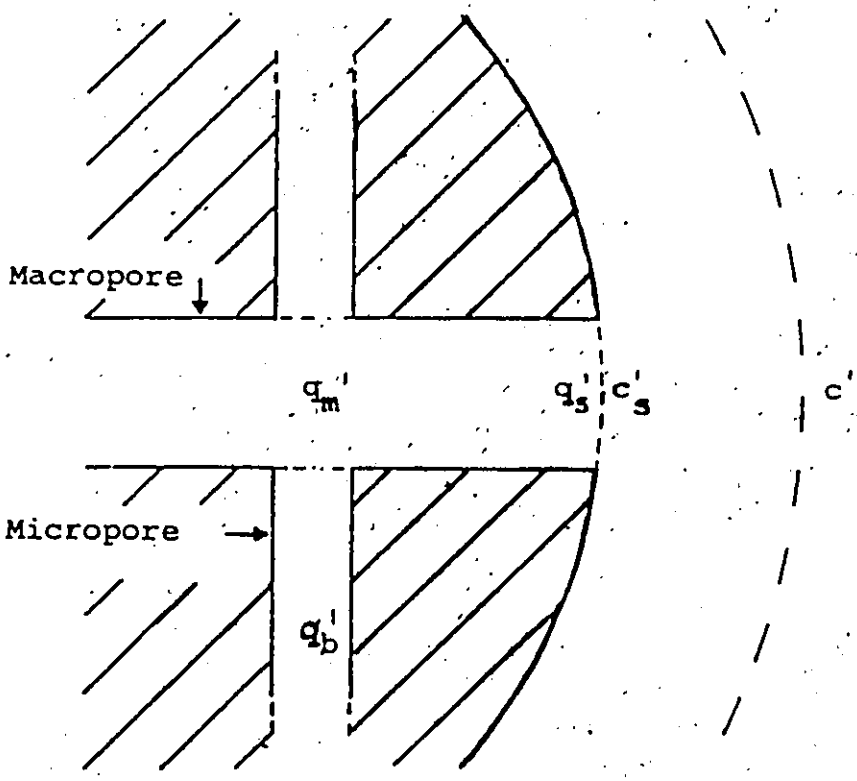

FIGURE 5.1 Conceptual Diagram of Proposed Branched Pore Model. (after Peel (1980))

film resistance, ii) adsorption onto the surface of the particle, iii) entrance to the particle via the macropores, iv)transport towards the interior of the particle within the macropores via surface diffusion, v) simultaneous transport onto the micropores or branch pores which are distributed throughout the particle. For a more detailed discussion refer to Peel (1980).

The equations describing the pertinent differential mass balances are:

Liquid Phase Balance in the Batch Reactor

$$\frac{dc'}{dt} = \frac{-(1-\varepsilon)}{\varepsilon} \cdot \frac{3k_f}{R_p} (c' - c_s') \qquad (5.1)$$

where c' = bulk liquid phase concentration, g/cm^3;

k_f = external mass transfer coefficient, cm/sec;

ε = liquid volume fraction in the kinetic bottles;

R_p = particle radius, cm;

c_s' = liquid phase concentration at the surface of the particles, g/cm^3; and,

t = time variable, sec.

Macropore Mass Balance

$$f \frac{\partial q_m'}{\partial t} = f \frac{D_s}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial q_m'}{\partial r}\right) - R_b \qquad (5.2)$$

in which f = fraction of the total particle capacity in the macropores;

q_m' = solid phase concentration in the macropores, g/g;

D_s = surface diffusivity in the macropores, cm^2/sec;

r = particle radial variable, cm; and,

R_b = local rate of transfer, g/g/t.

Micropore Mass Balance

$$(1-f)\frac{\partial q_b'}{\partial t} = k_b\,(q_m'-q_b') = R_b \qquad (5.3)$$

where q_b' = solid phase concentration in the branch pores; g/g; and,

k_b = pseudo mass transfer coefficient for transport to the branch pores.

Liquid Phase - Solid Phase Boundary Condition

$$f \cdot D_s \cdot \rho_c \left.\frac{\partial q_m'}{\partial r}\right|_{R_p} = k_f\,(c'-c_s') \qquad (5.4)$$

where ρ_c = carbon density of the carbon particles, g/cm^3.

Equation 5.4 is obtained by equating the liquid phase and solid phase fluxes at the surface and on the assumption that only the macroporous region is available for radial transport.

The initial and boundary conditions for this model are:

$$q_m'(r,0) = 0 \qquad (5.5)$$

$$q_b'(r,0) = 0 \qquad (5.6)$$

$$\frac{\partial q_m'}{\partial r}(0,t) = 0 \qquad (5.7)$$

$$q_m'(R_p,t) = g\{c_s'(t)\} \qquad (5.8)$$

Equation 5.8 stipulates that the solid phase concentration at the outer surface of the carbon grain is in equilibrium with the immediately adjacent liquid phase concentration. Thus $g\{c_s'\}$ is the isotherm model expression which is identified and calibrated by analyzing the batch isotherm data.

It should also be noted that the total solid phase concentration, q_T', at any point along the radius is

$$q_T'(r,t) = f \cdot q_m'(r,t) + (1-f) \cdot q_b'(r,t) \qquad (5.9)$$

To transform the model to a dimensionless form the following variables were used:

$$C = c'/c_o' \tag{5.10}$$

$$Q_m = q_m'/q_o' \tag{5.11}$$

$$Q_b = q_b'/q_o' \tag{5.12}$$

$$\theta = D_s \cdot t / (R_p)^2 \tag{5.13}$$

$$\beta = r / R_p \tag{5.14}$$

where c_o'= initial liquid phase concentration, g/cm^3; and,

q_o'= solid phase concentration in equilibrium with c_o', g/g.

And equations 5.1 to 5.8 became

$$\frac{dC}{d\theta} = FI \cdot BIF \cdot (C-C_s) \tag{5.15}$$

$$\frac{\partial Q_m}{\partial \theta} = \frac{1}{\beta^2}\frac{\partial}{\partial \beta}\left(\beta^2 \frac{\partial Q_m}{\partial \beta}\right) - \frac{BIP}{f}(Q_m-Q_b) \tag{5.16}$$

$$\frac{\partial Q_b}{\partial \theta} = \frac{BIP}{(1-f)} \cdot (Q_m-Q_b) \tag{5.17}$$

$$\left.\frac{\partial Q_m}{\partial \beta}\right|_{\beta=1} = \frac{BIF \cdot BIGF}{3F}(C-C_s) \tag{5.18}$$

where $BIF = 3 \cdot k_f \cdot R_p / D_s$ (5.19)

$BIP = k_b \cdot (R_p)^2 / D_s$ (5.20)

$FI = -(1-\varepsilon) / \varepsilon$ (5.21)

$$BIGF = \frac{c_o}{\rho_c\, q_o'} \tag{5.22}$$

The initial and boundary conditions became

$C(0) = 1.$ (5.23)

$Q_m(\beta,0) = 0.$ (5.24)

$Q_b(\beta,0) = 0$ (5.25)

$$\frac{\partial Q_m}{\partial \beta}(0,t) = 0. \qquad (5.26)$$

$$Q_m(1,t) = g(c_s') \qquad (5.27)$$

Equations 5.16 through 5.27 were solved using orthogonal collocation (Villadsen and Stewart (1967)) which transforms these partial differential equations (PDEs) into a set of ordinary differential equations (ODEs) in time. This is desirable because ODEs can be integrated numerically by techniques, such as the Runge-Kutta method, which are more accurate than the solution of PDEs by finite difference analogues. If a small size integration step, h, is used, the error in the solution of ODEs is proportional to h^4, while that of the PDEs is proportional to h or h^2. This permits the use of larger step size, which results in a faster solution (Crittenden et al, 1980). Appendix F1 presents a brief description of orthogonal collocation and its application to equations 5.16 and 5.27. For a detailed description of this technique, refer to Villadsen and Stewart (1967).

Orthogonal collocation has been found successful by Crittenden et al (1980) and Thacker et al (1981) in solving a conventional surface diffusion model. It has also been used for a pore diffusion model (Liapis and Rippin (1977)) and the combined pore - surface diffusion model (Neretnieks (1976)).

A computer program, called SEAR5, which applies this technique to the dual rate model, is presented in Appendix F3. This program was tested using the phenol data and mass transfer coefficients by Peel (1980) and it was found to yield very similar results (see Appendix F2). The numerical integration was carried out by the IMSL (1982) routine DGEAR which adjusts the time steps so as to meet error constraints.

The above simulations using orthogonal collocation used two

internal collocation points, as increasing the number of points to three changed the solution only in the fourth significant figure. Thacker et al (1981) observed similar results. Liapis and Rippin (1977) and Neretnieks (1976) found it necessary to use six internal collocation points to obtain the same accuracy, but this was thought to be caused by the slightly different nature of their models (i.e., pore diffusion). However, in using the collocation technique with the data generated in this study, it was found that the TCEA and FRW simulations required respectively 4 and 5 internal collocation points before an additional point introduced a change in only the fourth significant figure. Thus five internal collocation points were chosen for all the calculations. The large difference in the number of collocation points required to obtain the same accuracy for the phenol data of Peel (1980) and the data in this study were not studied further. However, there were substantial differences in the values of the concentrations, the mass transfer coefficients, and the isotherm coefficients, which indicates the need for careful pretesting before using orthogonal collocation in any application.

5.2 APPLICATION OF THE MODEL TO THE SINGLE COMPONENT BATCH KINETICS

The single component kinetics experiments were regressed using a non linear least square routine (UWHAUS, McMaster University Computing Centre). The data of the two solutes were analyzed using both the Peel (1980) dual rate model and the homogeneous solid surface diffusion model.

5.2.1 Trichloroethane Kinetics

The data of the 45 point 1,1,2-trichloroethane batch kinetics tests are tabulated in Appendix G1, and are shown in Figure 5.2. As it

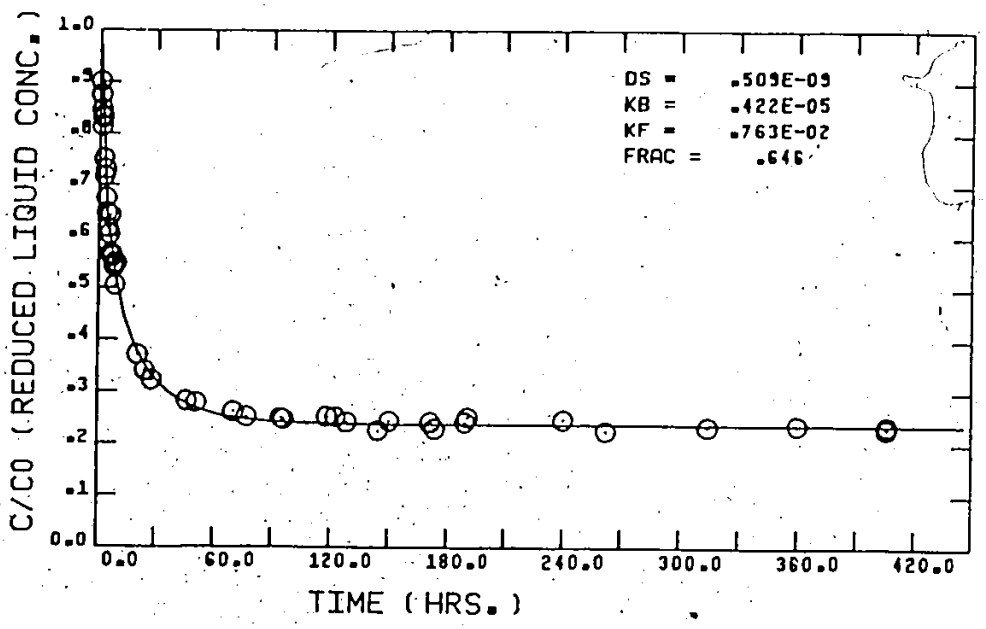

FIGURE 5.2 TCEA Kinetics Simulated by the Dual Rate Model.

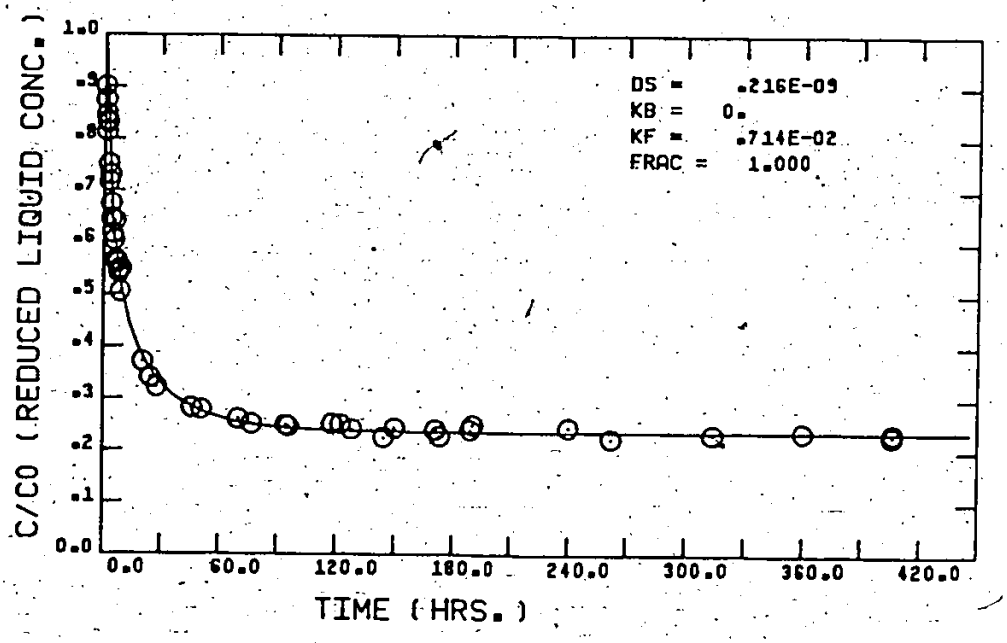

FIGURE 5.3 TCEA Kinetics Simulated by the HSSD Model.

can be seen from this graph, the adsorption occurs relatively rapidly, reaching equilibrium in about four days. The adsorption capacity observed in this test was about 28 percent larger than expected from the PAC isotherms. This was surprising since the adsorption capacity was expected to be the same or slightly higher for the PAC, because of its slightly higher surface area. Two sets of carbon dosages of both PAC and GAC were tested to confirm this finding. These tests confirmed the higher capacity of the GAC and they showed that both isotherms had the same slope. Lee and Snoeyink (1980) had similar results with a humic acid solution adsorbed onto F-400. The 40-60 mesh fraction they used in the kinetic experiments was obtained by sieving and the powdered activated carbon used in the batch isotherms was obtained by pulverizing the GAC larger than 40 mesh. Based on this, Lee and Snoeyink (1980) speculated that due to their size the larger GAC particles were not completely activated to their centres, resulting in a PAC which was less adsorptive per unit mass than the 40-60 mesh GAC. Since in this study the PAC was also obtained by grinding the GAC particles larger than 40 mesh, the same explanation may be applicable. To eliminate the possibility of a lesser degree of activation in larger carbon particles, it is recommended that the PAC used for isotherms be obtained by grinding the GAC to be used in the kinetic experiments.

As it was not possible to repeat the isotherms with GAC, the adsorption isotherms used in the kinetic modeling was adjusted to the higher adsorption capacity. The tests conducted indicated that the exponent of the Freundlich isotherm for the GAC was the same as that of the PAC, thus the "k" coefficient was increased by the ratio of the observed loading to the expected loading from the PAC.

The results of the regression of these data are shown in Figures 5.2 and 5.3, and in Table 5.1. As can be seen from these graphs, there is almost no difference between the simulations by the two models. The similarities are also reflected in Table 5.1, as the sums of squares only differ by 1.5 percent. The confidence intervals of the parameters of the homogeneous solid surface diffusion (HSSD) model are about 17% of the estimated parameters, while those of the dual rate model are much larger. For example, the confidence interval of f (i.e., the fraction of the adsorption capacity in the macropores) almost reaches up to 1, and the confidence interval of the surface diffusion ranges into negative values. Due to these results, the branch pore transfer resistance is not required, and the HSSD model was chosen to represent the kinetics of this compound.

Since there was no kinetic information in the literature for this particular compound, only order of magnitude comparisons with similar compounds are possible. Weber and Pirbazari (1983) studied the kinetics of carbon tetrachloride adsorption with an initial concentration of 186 ug/ℓ. These investigators found that the above experiment was described by the HSSD model with $D_s = 3.0 \times 10^{-10}$ cm^2/sec, in essential aggreement with the value obtained in this study (i.e., 2.16×10^{-10} cm^2/sec). Since the film mass transfer coefficient is a function of the hydrodynamics of the kinetic apparatus, the values of k_f obtained by this study and those obtained by Weber and Pirbazari (1983) should not be compared.

5.2.2 Fauquier River Water Organics

The data of the kinetics test of the background organics are tabulated in Appendix G2 and are shown in Figure 5.4, as a reduced

TABLE 5.1 Regressed Parameter Values and their 95% Confidence Intervals from the TCEA Batch Kinetic Test

	PEEL'S DUAL RATE MODEL	HSSD MODEL
Sum of squares	0.12783 E-1	0.12975 E-1
k_f	7.610 E-3 (5.485E-3 - 9.735E-3)	7.144 E-3 (5.708E-3 - 8.579-3)
D_s	5.093 E-10 (-8.393E-11 - 1.1103E-8)	2.165 E-10 (1.857E-10 - 2.473E-10)
f	0.6460 (0.3461 - 0.9459)	1.0
k_b	4.220 E-5 (4.215E-6 - 4.225E-6)	0.0

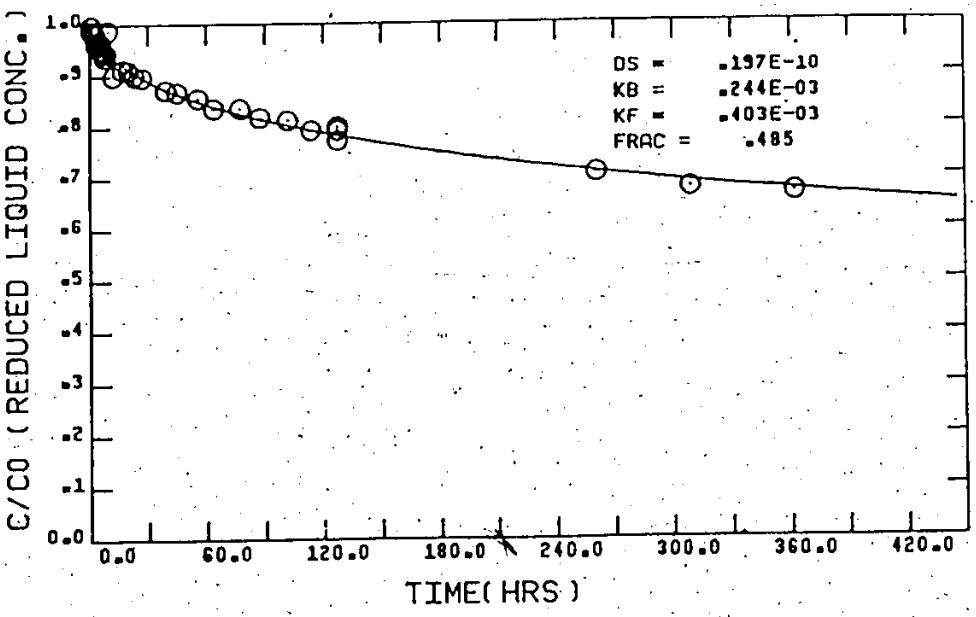

FIGURE 5.4 Regression of FRW Batch Kinetics with the Dual Rate Model.

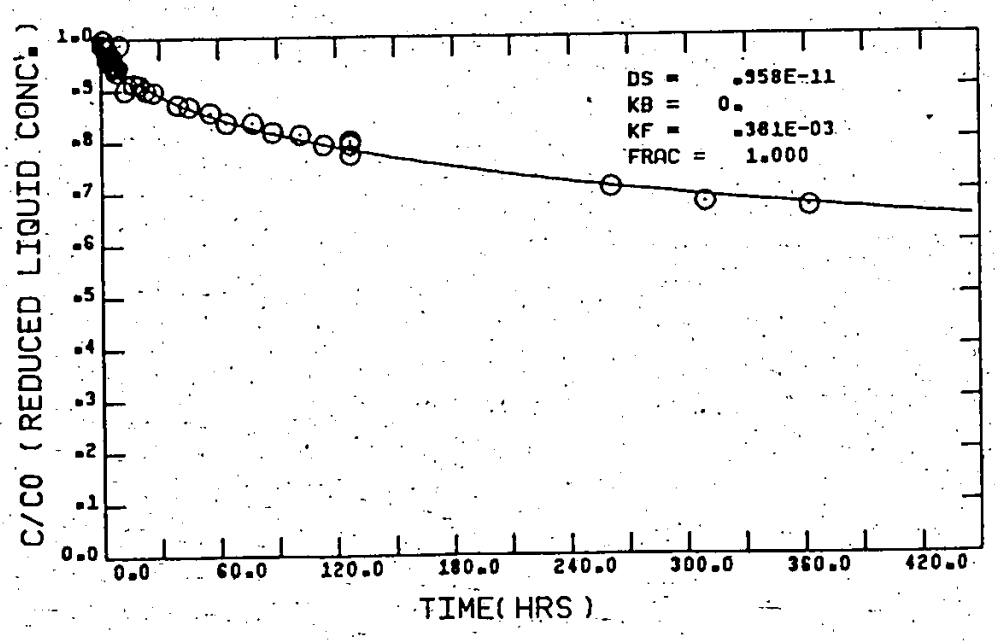

FIGURE 5.5 Regression of FRW Batch Kinetics with the HSSD Model.

concentration versus time graph. The line in the graph is the result of the regression analysis utilizing Peel's dual rate model.

The adsorption of these organics was very slow. In fact, the equilibrium liquid phase concentration for the conditions of the test conducted was 1.769 mg TOC/ℓ (or c/c_o = 0.359), and after two weeks the liquid phase concentration had only dropped to about 3.10 mg TOC/ℓ (or c/c_o = 0.65). Months of contact are probably required to reach equilibrium. This slowness is comparable to that observed by Peel (1980) and Randtke and Snoeyink (1983).

Figure 5.5 shows the results of the regression using the HSSD model and Table 5.2 shows the regressed values of the coefficients and their confidence intervals. Surprisingly, the HSSD model yielded very similar simulations to that of the dual rate model. Table 5.2 also confirms these results as the sum of squares of the two models differ by only 2.5 percent. The magnitude of the confidence intervals followed a similar pattern to those of the TCEA kinetics. The values of D_s for the background organics obtained with both models are an order of magnitude lower than those for TCEA despite the fact that humic concentrations are one order of magnitude higher than those of TCEA. Considering the general trend of decreasing values of D_s with decreasing concentration, as reported in literature, the background organics of this study adsorb very slowly. The HSSD model was chosen since it represents the data virtually as well as the dual rate model, and it requires a smaller computational effort. The quality of the fit by the HSSD model was somewhat surprising in light of Peel's findings for treated lake water. However, it should be noted that these results indicate that the slow adsorption mechanism represents virtually all of the adsorption

TABLE 5.2 Regressed Parameter Values and their 95% Confidence Intervals from the FRW Organics Batch Kinetic Test

	PEEL'S DUAL RATE MODEL	HSSD MODEL
Sum of squares	5.03189 E-3	5.0459 E-3
k_f	4.033 E-4 (3.820E-5 - 7.684E-4)	3.811 E-4 (1.972E-4 - 5.65E-4)
D_s	1.971 E-11 (-1.711E-10 - 2.105E-10)	9.579 E-12 (8.644E-12 - 1.051E-11)
f	0.4850 (-4.256 - 5.226)	1.0
k_b	2.443 E-4 (5.341E-5 - 4.352E-4)	0.0

observed.

Lee et al (1982) studied the kinetics of the adsorption of three different humic solutions onto the same brand of carbon used in this study. Their regression of the data by the HSSD model yielded values of 1.7, 2.3, and 2.7 X 10^{-11} cm^2/sec which are only slightly higher than the 0.96 X 10^{-11} cm^2/sec obtained for FRW. This represents fairly close agreement considering the likely differences between the humics of different sources.

As mentioned earlier, the adsorption mechanism responsible for the slow adsorption was hypothesized to also cause irreversible adsorption because both phenomena are caused by steric or chemical restrictions. The limited data from these kinetic experiments confirm this hypothesis. The TCEA adsorption, which showed no slow adsorption, was completely reversible, whereas the adsorption of the background organics, which occurs almost entirely by the slow adsorption mechanism, was shown to be completely irreversible. Based on these results, Bersillon (1984) tested the adsorption of phenol and found that 70 percent of the adsorption was both irreversible and attributable to the slow adsorption mechanism. Herzing et al (1977) conducted a column run with 2-methylisoborneol and obtained a breakthrough typical of those of slow adsorbing compounds. A change in feed to distilled water resulted in almost no desorption. These findings indicate that the slow adsorption mechanism and irreversible adsorption appear to be related, but further confirmation with a wider range of compounds is required.

5.3 MULTICOMPONENT KINETIC MODELS

As discussed in section 2.2.4, most multicomponent kinetic models are identical to single component models, except that there is a

set of equations to represent each compound and they are linked by the competitive isotherm model at the interface boundary. However, most models assume no diffusional interactions, and they are generally applied without checking this assumption. The studies in this area found that significant diffusional interactions exist when the single component diffusivities varied by a factor greater than 2 (Crittenden (1976), Mathews and Weber (1980) and Merk et al (1980)). Since in this case they differ by a factor of 23, the intraparticle cross diffusional interactions would probably have to be considered in order to simulate the data. Therefore they will be included in the competitive adsorption model. In addition the competitive adsorption model will be based on the HSSD model as it was shown to be more practical for this particular application.

The bisolute model is then comprised of liquid phase balances (equation 5.1), intraparticle balances and the boundary conditions for both solutes.

Intra Particle Balance with Diffusional Interactions

$$\frac{\partial q_i'}{\partial t} = \frac{D_{s_{ii}}}{r^2}\frac{\partial}{\partial r}\left[r^2 \frac{\partial q_i'}{\partial r}\right] + \sum_{\substack{j=1 \\ j\neq i}}^{NC} \frac{D_{s_{ij}}}{r^2}\frac{\partial}{\partial r}\left[r^2 \frac{\partial q_j'}{\partial r}\right] \qquad i=1,NC \tag{5.28}$$

where i = counter of the solute in question;

j = counter of the other solutes;

$D_{s_{ii}}$ = single solute diffusivity, cm^2/sec; and,

$D_{s_{ij}}$ = cross diffusivity, cm^2/sec.

Liquid Phase - Solid Phase Boundary

$$D_{s_{ii}} \cdot \rho_c \cdot \left.\frac{\partial q_i'}{\partial r}\right|_{R_p} = k_{f_i}\,(c_i' - c_{s_i}') \tag{5.29}$$

The initial and boundary conditions are as follows:

$$q_i'(r,0) = 0 \tag{5.30}$$

$$\frac{\partial q_i'}{\partial r}(0,t) = 0 \tag{5.31}$$

$$q_i'(R_p,t) = g(c_{s_i}'(t)) \tag{5.32}$$

The function of $g(c_{s_i}')$ in equation 5.32 is described by the MSCAM model which was chosen from the analysis of the bisolute isotherm data.

This model can then be transformed to a dimensionless form by the following variable changes.

$$C_i = c_i' / c_{o_i}' \tag{5.33}$$

$$Q_i = q_i' / q_{o_i}' \tag{5.34}$$

$$\theta = D_{s_{11}} t / (R_p)^2 \tag{5.35}$$

$$\beta = r / R_p \tag{5.36}$$

And equations 5.1, 5.28 and 5.29 for component 1 become

$$\frac{dC_1}{d\theta} = COR1\ (C_1 - C_{s_1}) \tag{5.37}$$

$$\frac{\partial Q_1}{\partial \theta} = \frac{1}{\beta^2}\frac{\partial}{\partial \beta}\left(\beta^2 \frac{\partial Q_1}{\partial \beta}\right) + CDS12 \cdot \frac{1}{\beta^2}\frac{\partial}{\partial \beta}\left(\beta^2 \frac{\partial Q_2}{\partial \beta}\right) \tag{5.38}$$

$$\left.\frac{\partial Q_1}{\partial \beta}\right|_{\beta=1} = CON1 \cdot (C_1 - C_{s_1}) \tag{5.39}$$

and for component 2

$$\frac{dC_2}{d\theta} = COR2\ (C_2 - C_{s_2}) \tag{5.40}$$

$$\frac{\partial Q_2}{\partial \theta} = CDS22 \cdot \frac{1}{\beta^2}\frac{\partial}{\partial \beta}\left(\beta^2 \frac{\partial Q_2}{\partial \beta}\right) + CDS21 \cdot \frac{1}{\beta^2}\frac{\partial}{\partial \beta}\left(\beta^2 \frac{\partial Q_1}{\partial \beta}\right) \tag{5.41}$$

$$\left.\frac{\partial Q_2}{\partial \beta}\right|_{\beta=1} = CON2 \cdot (C_2 - C_{s_2}) \tag{5.42}$$

where $COR1 = \dfrac{-(1-\varepsilon)}{\quad} \cdot 3k_{f_1} / D_{s_{11}}$ (5.43)

$$COR2 = \frac{-(1-\varepsilon)}{\varepsilon} \cdot 3k_{f_2} / D_{s_{11}} \qquad (5.44)$$

$$CDS12 = D_{s_{12}} \cdot q_{o2}' / (D_{s_{11}} q_{o1}') \qquad (5.45)$$

$$CDS22 = D_{s22} / D_{s_{11}} \qquad (5.46)$$

$$CDS21 = D_{s_{21}} \cdot q_{o1}' / (D_{s_{11}} q_{o2}') \qquad (5.47)$$

$$CON1 = \frac{c_{o1}'}{\rho_c \cdot q_{o1}'} \cdot \frac{k_{f1} \cdot R_p}{D_{s11}} \qquad (5.48)$$

$$CON2 = \frac{c_{o2}'}{\rho_c \cdot q_{o2}'} \cdot \frac{k_{f2} \cdot R_p}{D_{s11}} \qquad (5.49)$$

The initial and boundary conditions became

$$C_f(0) = 1.0 \qquad (5.50)$$

$$Q_f(\beta,0) = 0 \qquad (5.51)$$

$$\frac{\partial Q_f}{\partial \beta}(0,t) = 0 \qquad (5.52)$$

$$Q_f(1,t) = g(C_{s_f}) \qquad (5.53)$$

Equations 5.37 and 5.42 were solved by orthogonal collocation in the same manner as the single component model. The computer program which solves the above equation to simulate the bisolute batch experiment is listed in Appendix F4.

5.4 SIMULATION OF THE BISOLUTE BATCH KINETICS EXPERIMENT

The results of this experiment are listed in appendix G3 and they are shown in Figures 5.6 and 5.7. These figures also show the model predictions obtained when diffusional interactions are not assumed. As can be seen, there are some differences between the actual and predicted concentration histories. The adsorption of TCEA (Figure 5.6) occurs faster, as if the FRW organics (Figure 5.7) push them, and

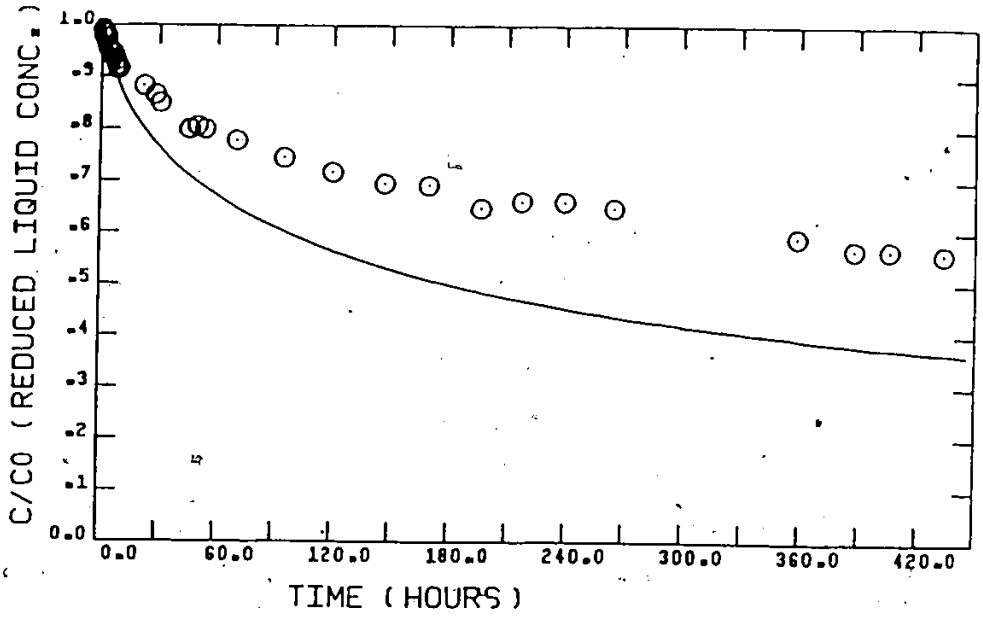

FIGURE 5.6 Kinetics of FRW Adsorption from a FRW/TCEA Solution and Prediction Based on a Model Without Diffusional Interactions.

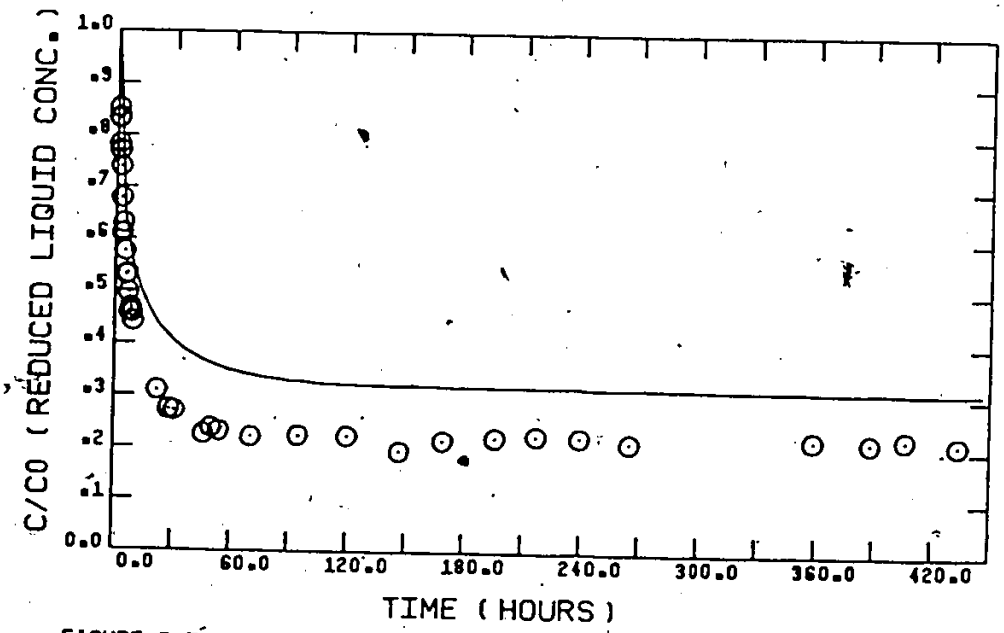

FIGURE 5.7 Kinetics of TCEA Adsorption from the Same FRW/TCEA and Prediction by a Model that Neglects Diffusional Interactions.

the FRW organics adsorb more slowly, as if the faster adsorbing TCEA is impeding the adsorption process. This type of behaviour is similar to that observed by Mathews and Weber (1980) in a system where the stronger adsorbing compound also diffuses substantially more slowly than the weaker adsorbing compound. Mathews and Weber (1980) used dodecyl benzene sulfonate (DBS) as the stronger adsorbing compound, and phenol as the weaker adsorbing compound which had a surface diffusivity about 14 times larger than DBS.

The kinetics data in this study was then regressed to the bisolute model with diffusional interactions within the particle. The regression was carried out with the multiresponse regression algorithm developed by Jutan (1976) which was discussed earlier. It is of interest that the regressed values of the cross diffusion coefficients (Table 5.3) were not quite as expected. FRW was considered as component no. 1 and TCEA as component no. 2 in the bisolute batch kinetics, thus D_{s12} is the cross diffusion coefficient of FRW resulting from the diffusion of TCEA. As the adsorption of FRW was slower than predicted when diffusional interaction are neglected, the regressed cross diffusion coefficient, D_{s12}, was expected to be negative. A similar comparison for TCEA, indicated that D_{s21} should be positive. Table 5.3 shows the D_{s21} was positive as expected, however D_{s12} was also positive. Tests with negative values of D_{s12} produced good fits in the initial part of the experiment but increasingly poor ones thereafter. The positive values of D_{s12} demonstrates that the competitive adsorption interactions play an extremely important role in the kinetics. The results of this analysis yield the simulations shown in Figures 5.8 and 5.9, which are significantly better than those which do not account for

TABLE 5.3 Estimates of the cross diffusion coefficients regressed from the batch kinetic experiment and their 95% Confidence Interval

D_{S12}	D_{S21}
3.75 E-10 (3.74E-10 - 3.76E-10)	1.10 E-11 (1.10E-11 - 1.10E-11)

- D_{S12} = Cross diffusion coefficient of component 1 (FRW) as a result of the diffusion of component 2 (TCEA)

- D_{S21} = Cross diffusion coefficient of component 2 (TCEA) as a result of the diffusion of component 1 (FRW)

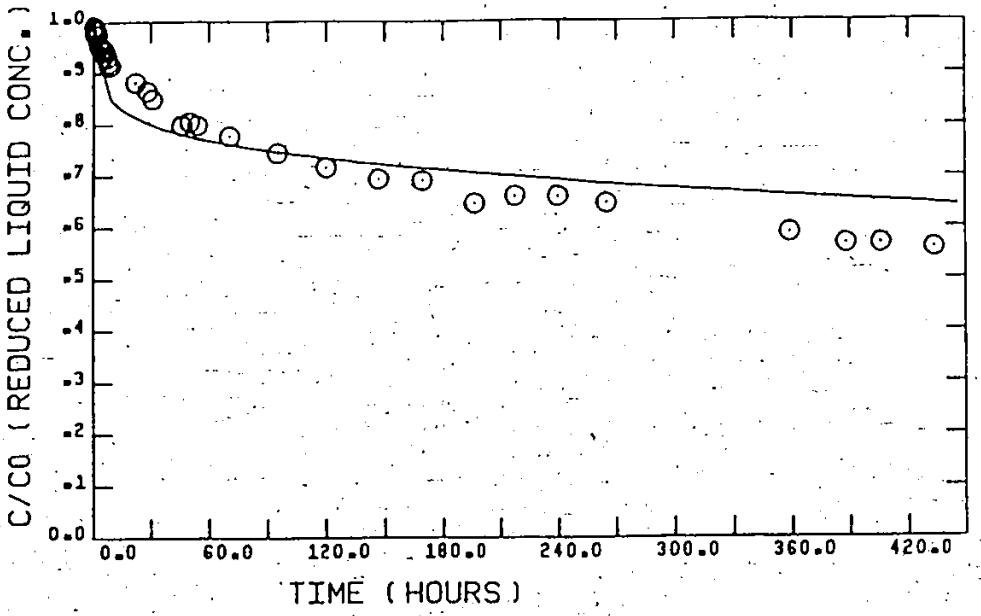

FIGURE 5.8 Simulation of the FRW Adsorption Kinetics from the FRW/TCEA Solution by the Model that Considers Diffusional Interactions.

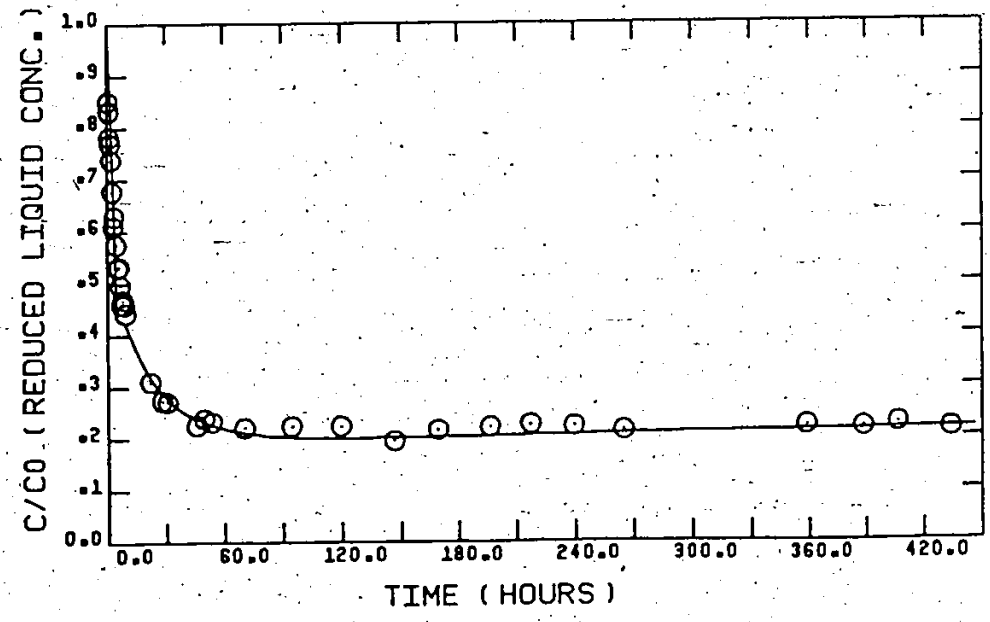

FIGURE 5.9 Simulation of the TCEA Adsorption Kinetics from the FRW/TCEA Solution by the Model that Considers Diffusional Interactions.

the diffusional interactions. Therefore, as expected, it is necessary to account for the diffusional interactions when dealing with solutes of fairly different diffusivities of the type encountered in drinking water applications.

CHAPTER SIX

COLUMN STUDY AND ENGINEERING IMPLICATIONS

6.1 COLUMN STUDY

The column study was divided into six phases with different feed concentrations. The different phases were intended to represent different situations encountered by water treatment GAC adsorbers treating a water source that receives occasional toxic spills. Although biodegradation is expected to be minimal since TCEA and the background organics are not easily biodegradable, some precautions were taken as outlined in chapter 3. In addition, a control column packed with sand was run in parallel with the GAC column. The effluent concentrations of the control column was essentially the same as that of the feed, indicating that adsorption onto the column system and biodegradation were insignificant. The data of the column study is reported in Appendix II.

6.1.1 Phase I

The initial phase of this experiment was intended to have a constant feed composed of 1:1 diluted FRW, spiked with TCEA to have a concentration of 500 µg/ℓ. Problems in the addition of TCEA resulted in some irregularities in the feed TCEA concentration.

The TCEA breakthrough (Figure 6.1) starts after 24 days, and by the 42nd day the effluent concentration exceeds that of the influent.

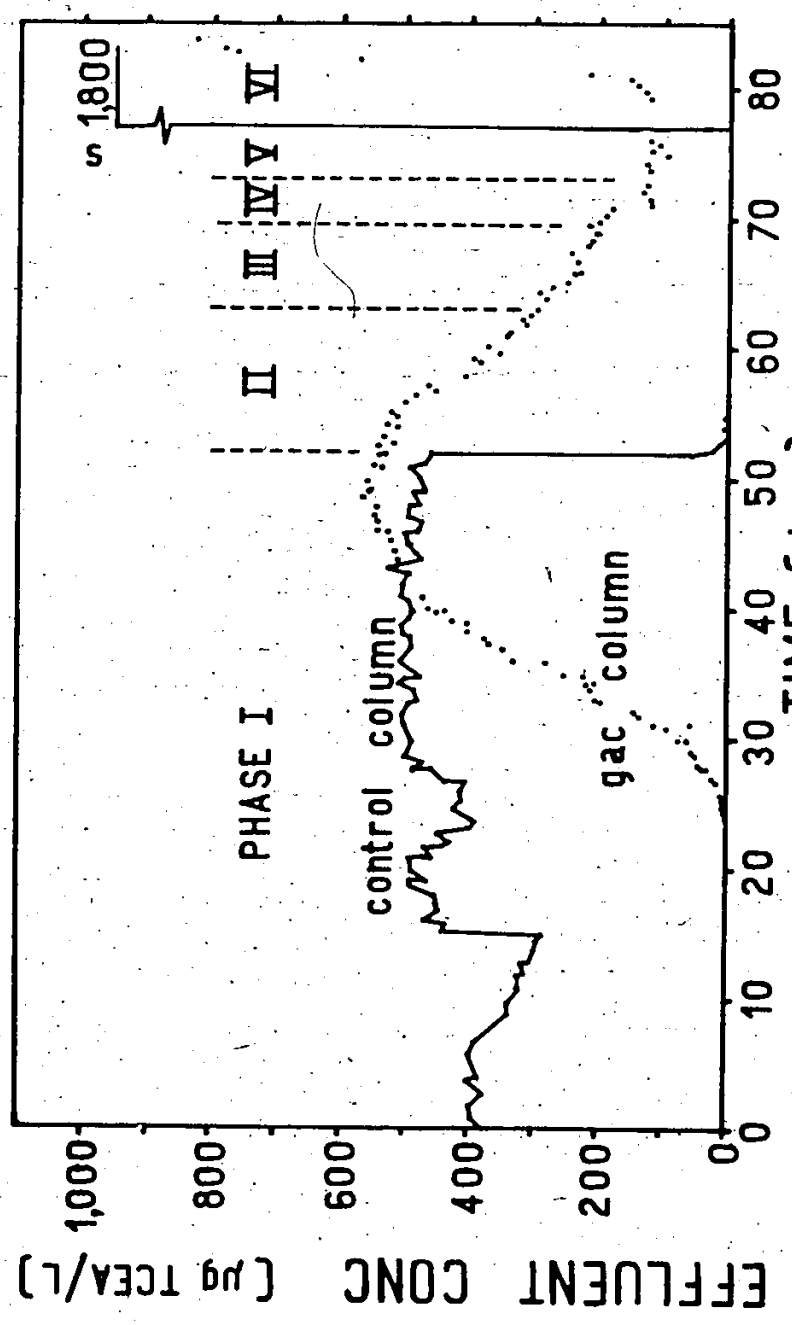

FIGURE 6.1 Trichloroethane Breakthrough Curve.

Based on equilibrium calculations, if the feed contained only TCEA the breakthrough would not be expected until about the 62nd day, which shows the significant impact of competition from the background organics. Based on the competitive isotherm, the breakthrough was expected after 30.5 days, which should be compared with the middle of the breakthrough which occurred at about 33 days. Thus the competitive isotherm gives a good general indication of the timing of the breakthrough. The TCEA overshoot observed after the 42nd day is caused by the displacement of TCEA by competition. This type of behaviour has been widely reported in pilot scale tests involving trihalomethanes (Suffet and McGuire (1980)).

The breakthrough of the natural organics (Figure 6.2) started almost immediately, and the effluent concentration increased relatively sharply during the first 12 days, followed by a more gradual increase in the effluent concentration. Even at the end of this phase which lasted over 7 weeks, the column still removed over 15 percent of the background organics. This type of breakthrough is typical of that found in water treatment applications. It is noteworthy that the breakthrough curve shows some small oscillations, which may be caused by the displacement effects between the different organic fractions that make-up the background organics.

Figures 6.3 and 6.4, respectively, present the average TCEA and TOC solid phase concentrations of the GAC versus time graphs. Based on the competitive isotherm for the column feed concentrations, the equilibrium solid loading would be 8.7 mg TCEA/g and 89.5 mg TOC/g. Thus, if this phase had continued, and if the rate of adsorption in Figure 6.4 had remained constant, equilibrium would not have been reached until run day 115. Since the kinetic model predicts a

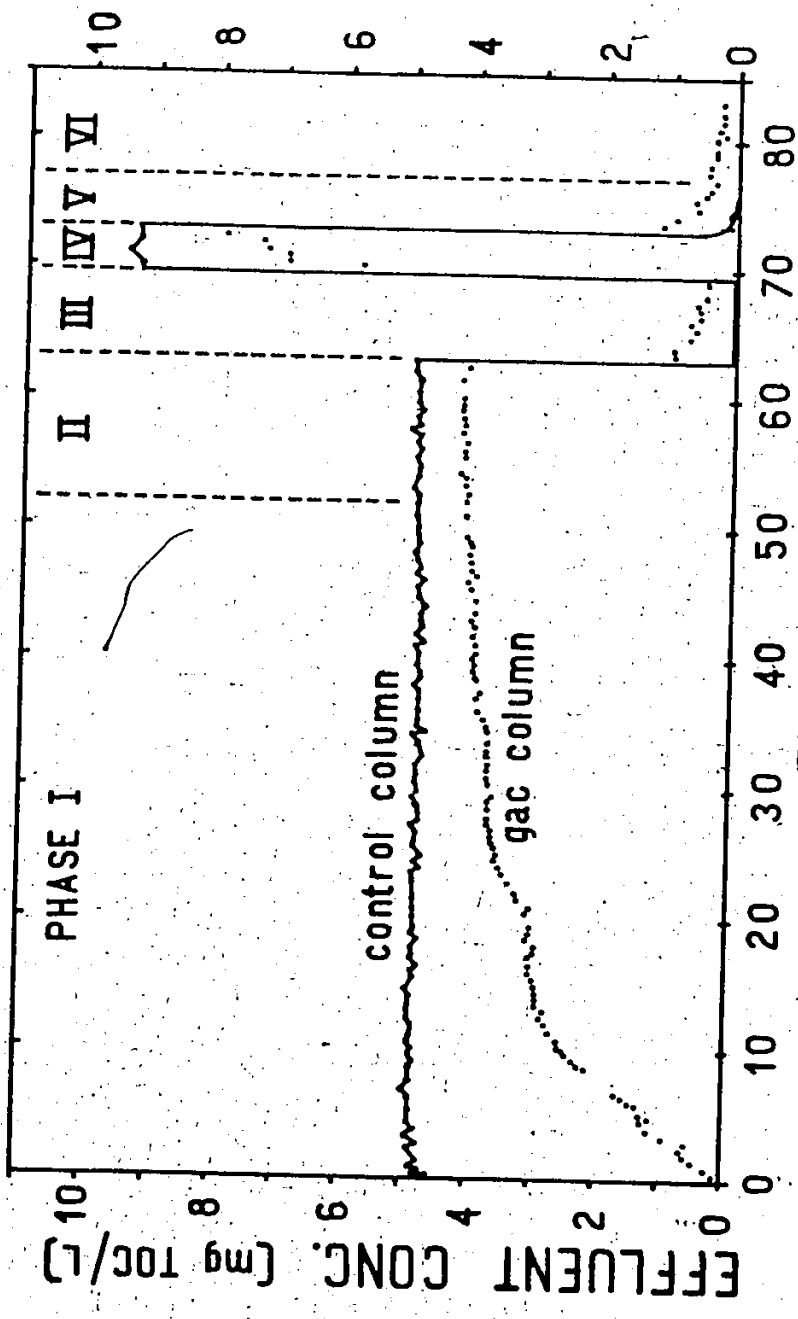

FIGURE 6.2 Breakthrough Curve of the FRW Organics.

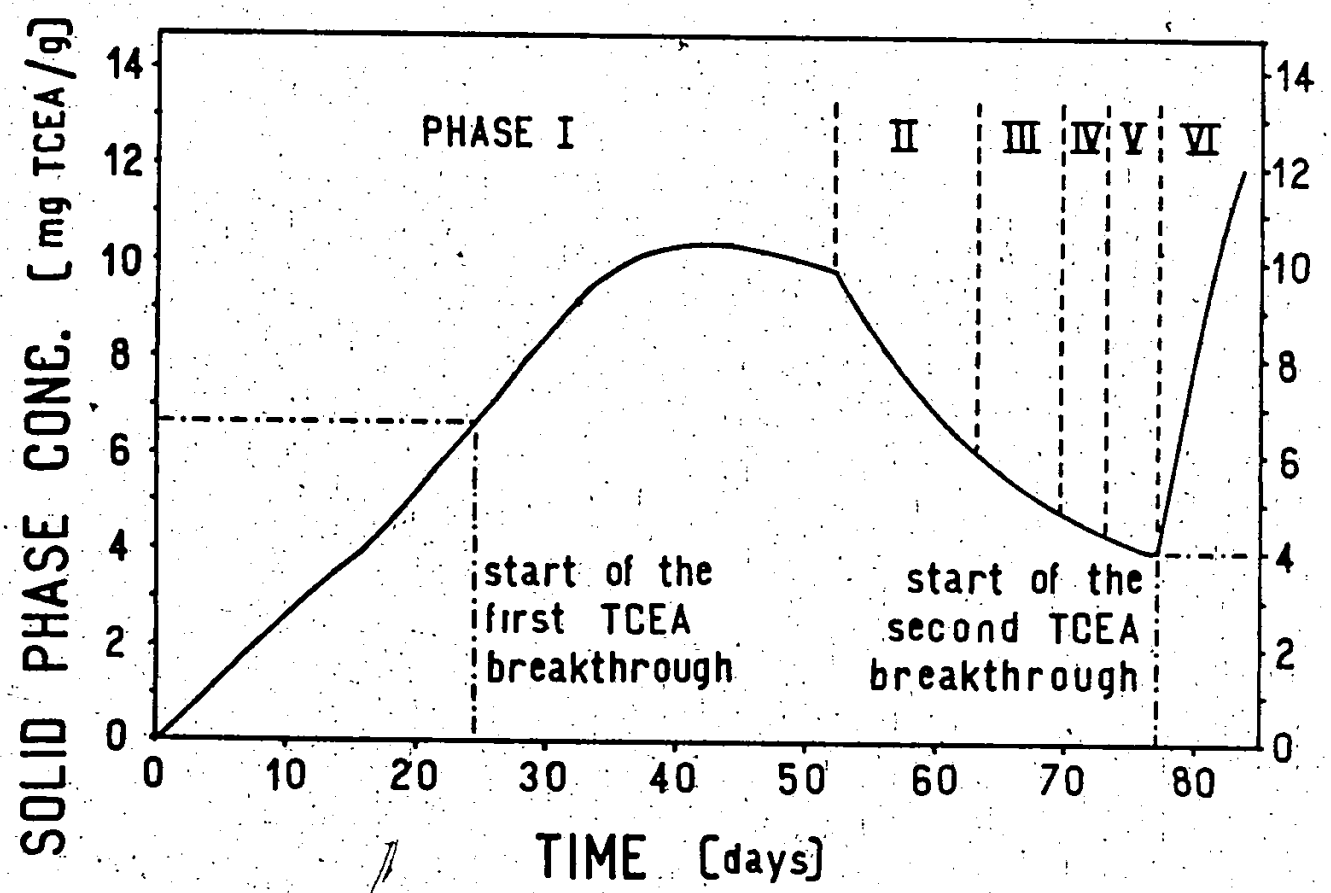

FIGURE 6.3 Average Trichloroethane Solid Phase Concentration of the Column GAC as a Function of Time.

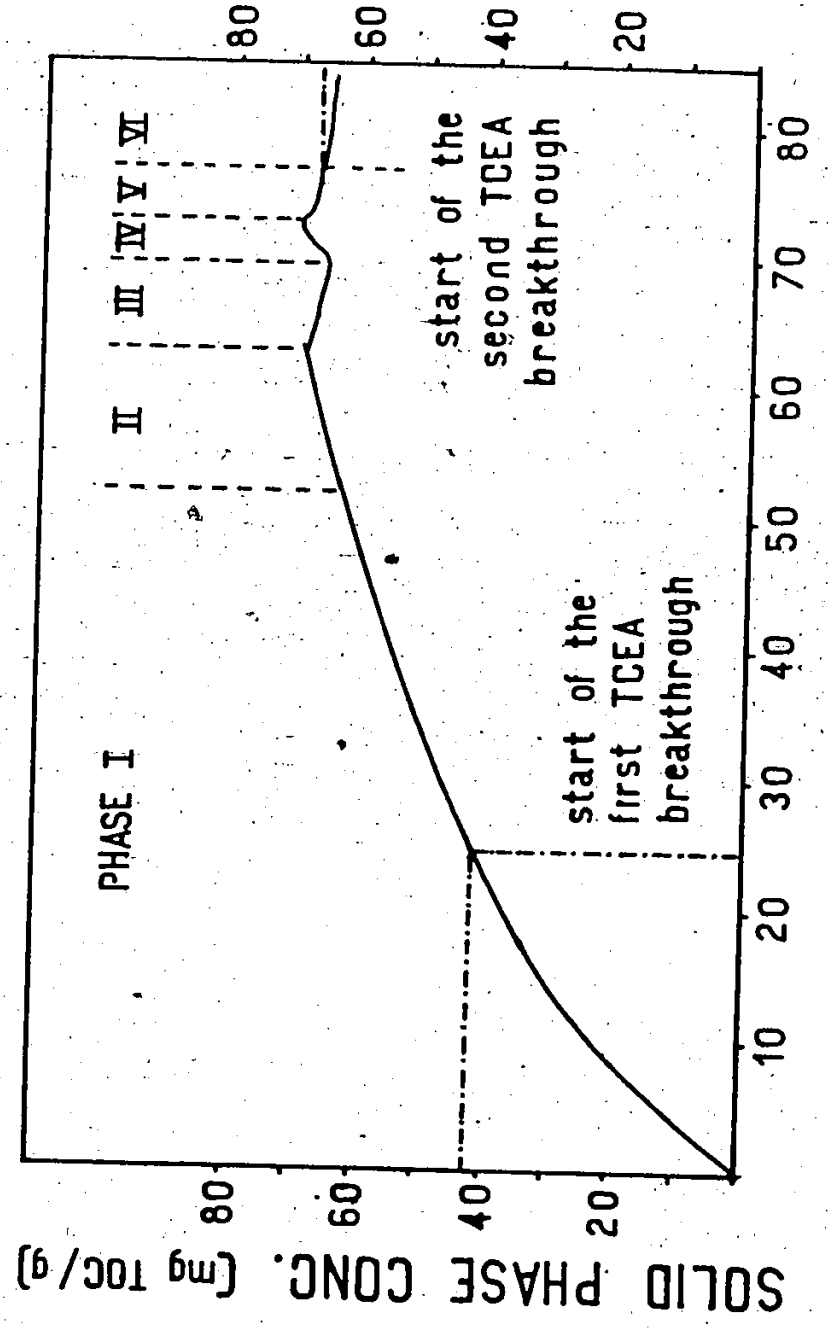

FIGURE 6.4 Average TOC Solid Phase Concentration of the Column GAC as a Function of Time.

decreasing rate of adsorption, it will take even longer to reach equilibrium. The TCEA overshoot would be of the same duration but, due to the long duration and the faster TCEA kinetics, the overshoot would not have been noticeable after approximately day 70 based on an equivalent set of calculations for TCEA.

6.1.2 Phase II

TCEA was not added during this phase, so the feed was composed of the background organics with a concentration of approximately 5 mg/ℓ. Figure 6.1 shows that large quantities of TCEA desorbed during this phase, due to the drop in the feed concentration as well as the continuing competition with the background organics. The extent of the desorption was also illustrated by the average TCEA solid phase concentration of the GAC versus time graph (Figure 6.3). It shows that the loading during this phase dropped from 9.8 to 6.1 mg TCEA/g (or 38 percent) due to the desorption. This significant desorption was expected as the desorption isotherms showed that TCEA adsorption was fully reversible.

The FRW organics continued to adsorb at about the same rate as in the previous stage.

Equilibrium calculations indicate that had this phase continued, the eventual loading would have been 0 mg TCEA/g and 94.6 mg TOC/g. At the end of this phase the actual loadings were 6 mg TCEA/g and 69 mg TOC/g, thus the phase would have had to run much longer to reach equilibrium. Calculations analogous to those in section 6.1.1 show that it would have taken at least 125 run days. This run time might seem somewhat short but it should be noted that the FRW was not coagulated as it would be in a water treatment plant, and coagulation has been shown

to substantially improve the activated carbon's adsorptive capacity for humics (Lee et al (1981) and Weber and Jodellah (1985)).

6.1.3 Phase III

The feed in this stage of the testing was buffered and filtered OFW, so as to cause both compounds to desorb. The TCEA continued to desorb at approximately the same decreasing rate as shown by the TCEA loadings in Figure 6.3. As expected from the highly irreversible desorption isotherms, there was only limited desorption of the background organics (Figure 6.2). The average TOC solid phase concentration versus time graph (Figure 6.4) shows that the loading only decreased from 69.5 to 66 mg TOC/g or only 5 percent. Equilibrium calculations for this phase predict an eventual loading of 0 mg TCEA/g and 64 mg TOC/g, thus there will be continued desorption.

6.1.4 Phase IV

Undiluted FRW was used as feed in this stage, to simulate a possible displacement of the adsorbed TCEA caused by an increase in the feed concentration of the background organics. Weber and Pirbazari (1983) observed this phenomenon in their bench scale test with carbon tetrachloride. This would be a critical situation at a water treatment plant. Surprisingly, the desorption of TCEA decreased substantially instead of increasing. A possible reason for these observations is that the FRW organic molecules being adsorbed partially block the desorption of TCEA. This hypothesis is supported by the observation of diffusional interactions in the bisolute batch kinetics test. Since Ds_{21} was found to be positive in section 5.4, then the increased rate of TOC adsorption could possibly reduce the rate of TCEA desorption.

The effluent TOC concentration increased fairly rapidly and it

removed approximately the same percentage of the organics as obtained towards the end of phase II.

6.1.5 Phase V

This is an intermediate phase where OFW was used as the feed. At this stage there was still a significant amount of desorption which occurred at an almost constant rate. Figure 6.3 shows that from the beginning of phase II to the end of phase V, 41 percent of the TCEA was desorbed. Again there was rather limited desorption of the background organics, however this mass was almost as much as that adsorbed during phase IV.

6.1.6 Phase VI

This phase was intended to see if a substantial toxic spill could desorb some of the previously adsorbed FRW organics. Accordingly, TCEA-spiked OFW was used as a feed. The experiment showed that there was very little desorption of the TOC (see Figure 6.4) and the substantial loading of the natural organics reduced the TCEA adsorption capacity to the point that a new breakthrough occurred immediately.

The importance of the adsorbed background organics is best illustrated by Figures 6.3 and 6.4, which present the average TOC and TCEA loading of the GAC column as a function of time. During phase I the loading reaches 6.6 mg TCEA/g before the TCEA appears in the effluent, while at the beginning of phase VI substantial quantities of TCEA are present in the effluent and the carbon loading is 4 mg TCEA/g. This large decrease in the TCEA adsorption capacity is directly attributable to competitive adsorption as the TOC loading increased from 42 mg TOC/g, at the start of the initial TCEA breakthrough, to 67 mg TOC/g, at the start of phase VI.

Competitive isotherm calculations predict that the equilibrium solid phase concentrations for this stage of the run would be 19.9 mg TCEA/g and 53.6 mg TOC/g. Based on these values and on the 4 mg TCEA/g at the start of this stage, the center of the breakthrough curve would be expected three days after the start of phase VI. As can be seen from Figure 6.1, the breakthrough starts as this phase begins, however the breakthrough is far from being completed 6 days after the start of this stage.

6.2 ENGINEERING IMPLICATIONS

The implications of this study to engineering practice can be classified into three categories: those applicable to column operation, those pertaining to the overall treatment scheme, and those related to adsorber modeling.

6.2.1 Implications to Column Operation

As demonstrated by the competitive isotherms, the TCEA adsorption capacity is significantly decreased by the competition with the background organics. As the operation of a water treatment adsorber proceeds in time, the carbon becomes increasingly loaded with the background organics. With time the increasing loadings, in conjunction with the competitive interactions, substantially reduce the adsorber's capacity to treat spills. As such, adsorbers utilized to protect a population from spills must be regenerated before the TOC removal signalled the need to do so. This is an important practical implication of this study, and it was confirmed by the column run. This behaviour will apply to other weakly adsorbing toxic compounds such as benzene and chloroform. Based on the work with pesticides by Robeck et al (1965) and with chlorophenols by Murin and Snoeyink (1979), similar behaviour

is also expected for stronger adsorbing compounds. For these compounds the effect might not be as noticeable because of the substantial capacities that remain available.

The background organics will have a more dramatic effect on the removal of weakly adsorbed toxic organics present in the feed at all times, such as trihalomethanes in water treatment plants practicing prechlorination. This competition results in an earlier breakthrough of the toxic organic as shown by the column run.

The desorption of previously adsorbed toxic compounds at water treatment plants is an area of great concern. Phase IV of the column run studied such a situation. Based on the equilibrium experiments, the increase in the feed background organics was expected to increase the desorption of TCEA, but instead it resulted in a decrease (Figure 6.1). Figure 6.3 shows that the change in the TCEA solid phase concentration was not as drastic, but the rate of desorption continued to decrease at about the same rate as in the previous phases of the run. Since diffusional interactions were observed to slow down the adsorption of TCEA in competitive batch kinetics, it seems possible that they also lower the rate of desorption in phase IV of the column study. In light of the importance of this question, this area merits further research.

6.2.2 Implication to the Overall Treatment of Toxic Organics

Since the adsorption of the background organics has been shown by the desorption isotherms and by the column run to be virtually irreversible, it is practically impossible to reduce previously adsorbed background organics in order to improve the adsorption of the toxic organics. Thus to lessen the impact of the background organics, the best solution is to remove them prior to the adsorption process. The

simplest method is by optimizing the coagulation process for their removal, instead of the common practice of optimizing for turbidity removal which results in less than optimal treatment of the humics. Such improved pre-treatment would result in longer column runs, and probably in a lower overall treatment cost. In addition, if chlorination could be delayed until after coagulation and if coagulation is optimized for the removal of the background organics, the formation of THMs would be greatly reduced (Babcock and Singer, (1979) and Semmens and Field (1980)). This would reduce the need for adsorbers to remove trihalomethanes, and it would permit their efficient use for other toxic organics.

Another method of reducing trihalomethanes in the finished water is to reduce their formation by switching to chlorine dioxide or to ozonation in the pre-disinfection step (Lykins and DeMarco (1983)). Also more specific synthetic organics could be used instead of activated carbon if pre-chlorination is essential. Rohm and Hass have developed the carbonaceous adsorbent Ambersorb XE-340, which does not adsorb humic substances and is an excellent adsorbent of trihalomethanes and other synthetic organics. It should be noted that this adsorbent might have to be used in series with activated carbon to remove the trihalomethane precursors prior to post-chlorination (Chudyk et al (1979)).

6.2.3 Implications to Column Modeling

Several factors encountered in this study are of great importance in modeling water treatment plant adsorbers.

First, some adsorption sites do not appear to adsorb certain compounds. This requires that competitive adsorption models include additional non-competitive terms to account for this phenomenon.

Second, the background organics adsorbed almost irreversibly, thus separate desorption isotherms are required to permit proper modeling of column adsorbers. The occurrence of this phenomenon with different water sources warrants further investigation.

Third, the irreversibility appears to be linked to the slow adsorption mechanism. A better understanding of this relationship will possibly help obtain a mathematical relationship between the macroporous factor f obtained from the kinetic experiments and the coefficients g1 and g2 obtained from the desorption isotherms. This would eliminate the need to conduct desorption experiments. This is a preliminary finding that requires further verification.

Fourth, the diffusional interactions discussed in sections 5.4 and 6.2.3 are key factors in proper modeling of this type of application. This requires models with extra terms such as in equation 5.28.

CHAPTER SEVEN

CONCLUSIONS AND RESEARCH RECOMMENDATIONS

7.1 CONCLUSIONS

1. The presence of natural background organics greatly reduces the adsorption capacity of 1,1,2-trichloroethane. Thus it is highly desirable to remove the background organics by some method of pretreatment to fully utilize the carbon's capacity to remove toxic organics.

2. The background organics adsorb virtually irreversibly. Therefore, regardless of the changes in the column feed, the background organics loading of the GAC will increase with time. Given that these organics reduce the GAC's capacity to adsorb toxic substances, with time adsorbers become substantially less effective in treating toxic spills.

3. Two multi-component isotherm models, which assume that a fraction of the adsorption does not involve competition, were found to describe the data successfully.

4. In spite of the very slow adsorption of the background organics in the Fauquier River water, its kinetics were adequately described by the homogeneous surface diffusion model, once all of the adsorption was assumed to occur by slow adsorption.

5. The slow adsorption phenomenon, which is expected to occur in very small pores, appears to be related to the degree of reversibility of the adsorption. The background organics that adsorbed almost exclusively by

the slow mechanism were virtually not desorbable. On the other hand, TCEA, which adsorbed completely reversibly, did not show any slow adsorption.

6. Modeling the adsorption kinetics of 1,1,2-trichloroethane from a solution of background organics must consider cross diffusional interactions in order to properly describe the data.

7. Two very simple desorption isotherm models were tested and were found to satisfactorily describe the desorption from activated carbon previously loaded to many different levels.

7.2 RECOMMENDATIONS FOR FUTURE RESEARCH

1. Investigate the reversibility of the adsorption of the natural background organics of different water sources.

2. Extend the testing of desorption and batch kinetics to a wide array of compounds to further test the relationship between irreversibility and the slow adsorption mechanism.

3. Conduct further column tests to check the effect of higher background organic concentrations on the desorption of previously adsorbed toxic compounds. During the column run in this study, this type of situation surprisingly yielded a decrease in the desorption capacity, an effect which should be confirmed. The toxic organics studied should have different degrees of adsorbability.

4. Conduct adsorption - desorption tests at different temperatures to evaluate the contribution of chemical reactions (chemisorption) to the observed irreversible adsorption.

5. Conduct adsorption isotherms with PAC ground from different particle size GAC to determine if the particle size affects the degree of activation of the particles and thus their adsorption capacity.

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APPENDIX A1

EXTRACTION PROCEDURE

The extraction was carried out in Hypo vials (Pierce Chemical Co., Rockford, Ill.) with a nominal volume of 125 ml. The actual volume of each of these bottles was measured using a graduated cylinder and recorded. Since the water volume used in each extraction was known from the bottle volume and the volume of solvent added was constant, the concentration ratio was calculated fairly accurately. The solvent volume of 3 ml. and freespace volume of 2.5 ml. were chosen as a result of a preliminary study of the extraction efficiency. The extraction efficiency was about 62 percent. Since the standards were prepared in water solutions which were also extracted in order to get the calibration curve, the extraction efficiency was already considered when using the calibration curve.

The procedure utilized was as follows:

1. Rinsed the bottle twice with the sample.
2. Filled the bottle to the top.
3. Removed sample from the bottle using a disposable Pasteur pipette and a rubber bulb, and dump into an empty 10 ml. graduated cylinder until it has 5.5 ml. Return any excess sample left in the pipette to the extraction bottle.
4. Added 3.0 ml. of n-pentane to the extraction bottle using a 5

ml. gas tight syringe dedicated to this purpose.

5. Immediately covered the extraction bottle opening with a teflon coated septum disk (Pierce Chemical Co.). Placed aluminum seal (Pierce Chemical Co.) on top of the disk and crimped the seal.

6. Shaked the bottles for about 10 seconds and stored them upside down in a refrigerator.

7. Shaked the bottles in a Wrist Action Shaker (Burrell Corp., Pittsburgh, Pa.) wrist shaker for 30 minutes. Towards the end of the study, another wrist shaker became available, and no storage was required.

8. Transferred the extract, when the two phases had separated sufficiently, to a GC autosampler minivial and crimped close. The transfer was carried out with disposable Pasteur pipettes and a small rubber bulb.

APPENDIX A2

GAS CHROMATOGRAPH CONDITION

Gas Chromatograph	= Hewlett-Packard HP 5880
Column	= 30 m X 0.25 mm I.D. DB-1
Carrier	= He at 35 ml/min
Injection	= Splitless (30 seconds)
Septum Purge	= 4 ml/min
Detector	= Ni^{63} Electron Capture Detector
Make Up Gas	= 30 ml/min He
Integration	= Peak areas calculated by HP level IV integrator
Oven temperature	= 45°C isothermal
Injector temperature	= 150°C
Detector temperature	= 300°C
Attenuation	= 28
Injection volume	= 3µl performed by HP autosampler

APPENDIX A3

STANDARDS AND ERROR

A3.1 STANDARDS

The initial step of this procedure was to prepare a TCEA stock (35 ml. n-pentane + 0.5 ml. TCEA), followed by an intermediate stock (30 ml. acetone + 0.4 ml. TCEA stock). The n-pentane and acetone were measured using pipettes, while the TCEA and its stock were measured using microsyringes. The n-pentane was Infrared Spectroanalyzed (Fisher Scientific, Fairlawn, N.J.) and the acetone was HPLC grade (Caledon Laboratories, Georgetown, Ont.).

The standards were prepared in 1 L. volumetric flasks using buffered OFW spiked with a TCEA intermediate stock solution. A test showed that there was no difference in the extraction efficiency of standards prepared in OFW, buffered OFW or FRW. Ten different standards were prepared to cover the range 0.1 to 90.0ng TCEA / 3µl. pentane. The typical calibration curve (Figure A3.1) can best be described as two straight lines intersecting at approximately 15 to 30 ng.

A3.2 ERROR

Several times during this research, a standard or an isotherm solution was prepared in big enough volumes so that six extractions could be conducted. This permitted an evaluation of the error involved in the analysis. The majority of these analyses yielded standard

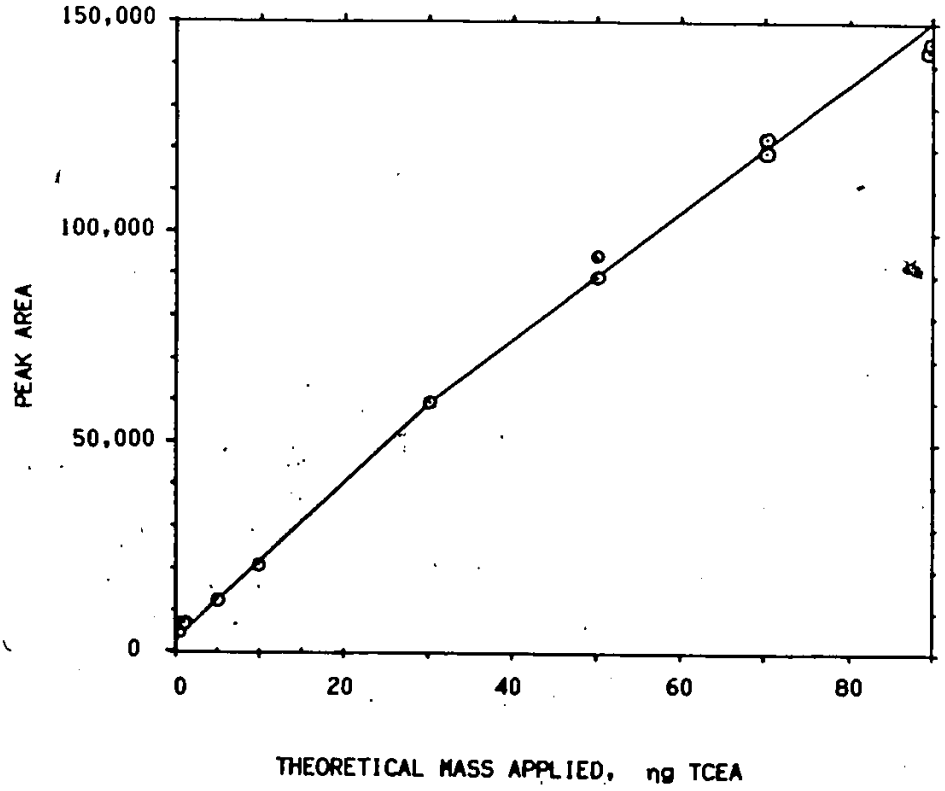

FIGURE A3.1 Typical Gas Chromatograph Calibration Curve for 1,1,2-Trichloroethane

deviations of 3 to 5 percent.

APPENDIX A4

GLASSWARE CLEANING

1. The bottles were filled with chromic acid and left standing for 2 to 3 hours.

2. The bottles were then rinsed three times with warm tap water.

3. The bottles were then twice filled and rinsed with OFW.

4. The bottles were then filled with OFW, covered to protect from dust, and left to stand overnight.

5. The bottles were then emptied and rinsed twice with OFW.

6. The bottles were then filled with OFW, covered, and left to stand overnight. The overnight soakings were intended to leach any possible remnants of chromic acid that may have been adsorbed onto the glass.

7. The isotherm bottles were then allowed to drip dry overnight. When dry, they were covered with aluminum foil and stored until required.

8. The extraction bottles were then rinsed twice with about 15 ml. HPLC grade acetone and dried overnight in a 105°C oven. The next day they were cooled, individually covered with aluminum foil, and stored until required.

APPENDIX B1

PROCEDURE FOR BATCH ISOTHERMS

In addition to all the bottles representing isotherm points, each experiment had two blanks and at least two controls. One blank consisted of organic free water (OFW) and the other of OFW plus a large dose of PAC, their purpose being to detect possible leaching or contamination problems due to the bottles or the PAC. The controls are used to determine the occurrence of losses and to calculate the solid phase concentrations. The procedure used for the bottles representing individual points in the isotherm relationship is as follows:

1. Cleaned the bottles, caps and teflon liners very well (See Appendix A4).

2. Placed teflon tape around the thread in the neck of the bottles, so that the cap and teflon liners can produce a tight seal.

3. Weighed the bottles with their caps on a Mettler PC 4000 balance (Mettler Instrument Corp., Highstown, N.J.).

4. Rinsed bottles twice with the solution to be used in the experiment.

5. Weighed an aluminum weighing dish on a Mettler HL-52 analytical balance and recorded the weight.

6. Calculated the target weight for the weighing dish + desired PAC weight.

7. Weighed the PAC to target weight with the analytical balance.

8. Slowly poured the PAC from the dish into the isotherm bottle by gently tapping it in. Great care was taken not to spill any PAC. When finished, the bottle was capped.

9. Reweighed the aluminum dish to account for the PAC that sticked to the dish.

10. Completed steps 5 through 9 for all the bottles.

11. The bottles were filled in a random order with the solution studied, so that if there are volatization losses during the filling process, the errors are randomized. The control bottles were included among the other bottles.

12. Filled the bottles as much as possible without overspill, which is paramount because there is always PAC on the surface of the liquid. The bubble left in the bottle aids the mixing when placed in the tumbler. The main drawback of having a bubble is the possible volatization of the solute. See appendix B5.

13. Reweighed the bottles to obtain the mass of solution in each bottle.

14. Placed all the bottles in the tumbler located in a temperature controlled ambient.

15. The bottles were allowed to tumble for at least 14 days to achieve equilibrium.

16. Upon the completion of the contact period, the PAC and the solutions were separated by pressure filtration. Pressure filtration minimizes the solute losses due to volatization. The filtration steps are outlined in Appendix B2.

17. Stored the filtrate destined for UV or TOC analysis in 5°C

refrigerator until analyzed. The extraction procedure for samples destined for TCEA analysis was started immediately.

APPENDIX B2

FILTRATION STEPS

The pressure filtration was carried out using 0.2μm pore size cellulose nitrate membrane filters (Sartorius, West Germany) and it was propelled by ultra high purity nitrogen. The filters were soaked in OFW at least overnight to extract leachable organics. The filter apparatus is constructed of stainless steel and it is operated in a batch mode when separating the carbon from the solution.

1. In between each filtration, I disassembled the filter and cleaned its parts with a brush and some OFW.

2. Assembled the apparatus without a membrane filter.

3. Rinsed the apparatus by passing two volumes (about 170 ml.) of OFW through it.

4. Carefully placed the membrane in position with tweezers.

5. Filtered a full volume of OFW. This served:

   a) to check for carbon fines leftover from the previous filtration because of improper cleaning; and

   b) to remove most possible leachable organics.

6. Repeated step 5.

7. Placed about 20 ml. of the sample solution in the filter. Disconnected apparatus in order to shake well, so that solution to be filtered was contacted with the entire filter apparatus. Reattached

apparatus and filter. Discarded filtrate.

8. Repeated step 7, but collected the filtrate into the TOC collection bottle or into the TCEA extraction bottle, using it for a rinse.

9. Filled the filter apparatus and filtered 20-40 ml of sample, using the filtrate for a second rinse of the collection bottles.

10. Filtered the required volume of sample into the collection bottles.

In each filtration section, the samples were ordered for filtration from low to high concentrations to reduce the possibility of contamination. Prior to each filtration section, the filter apparatus was taken completely apart, and was thoroughly washed in a hot soap solution. It was then rinsed with hot tap water and reassembled. Finally, the filter apparatus was set up in the semi batch mode with a membrane in place. Ten liters of OFW was passed through the filter to thoroughly rinse it.

APPENDIX B3

DESORPTION ISOTHERMS

As explained in section 3.5, these experiments were carried out with the PAC loaded during adsorption isotherms. The overall method followed in this study is essentially the same as that for the adsorption isotherm, except for the transfer of the PAC. This procedure will be discussed in detail as it was not discussed before, and it is the most critical part of the experiment.

1. The bottles for the desorption isotherm and the desorption solution (buffered OFW) were prepared before the end of the adsorption experiment.

2. In addition, the bottles were rinsed twice with this water previous to use.

3. A wash bottle was filled with the desorption solution.

4. As part of the final filtration step of the adsorption isotherm, all of the water in the isotherm bottle was filtered.

5. The desorption bottle with a large glass funnel on top was placed beneath the filter apparatus.

6. The adsorption bottle was rinsed with desorption solution to remove all of the PAC, and this water was then poured into the filter.

7. Step 6 was repeated until there was no PAC left in the adsorption bottle.

8. The water in the filter apparatus was filtered, the filtrate ending in the desorption bottle.

9. The bottom part of the filter was disassembled and the membrane filter with the PAC was placed in the glass funnel.

10. The interior of the filter apparatus was cleaned with a brush and the desorption solution. All of this water poured into the desorption bottle.

11. The carbon on the filter was washed down into the desorption bottle.

12. The funnel is then raised, so that the membrane filter, which still contained some PAC, could be placed into the desorption bottle with a pair of tweezers.

13. The funnel was then lowered on top of the desorption bottle, and the cleaning brush was thoroughly rinsed with the desorption solution.

14. The glass funnel was then rinsed clean. By this time, the desorption bottle had in it about 400 ml. of the desorption solution.

15. The bottle was filled and sealed. It was then placed in the tumbler, and the rest of the experimental procedure is identical to that of the adsorption procedure.

APPENDIX B4

PROCEDURE FOR BATCH KINETICS

This procedure is essentially the same as that outlined in appendix B1, except for the following modifications.

1) The first precaution was to determine the weight of water required to fill each isotherm bottle with water. This permitted the calculation of the target GAC mass to be added to each bottle in order to have a constant carbon dosage.

2) The second key step was to use distilled water to wash all the grains of GAC from the weighing dish into the isotherm bottle. This increased the uniformity of the carbon masses added. The bottles were then filled up to 5 percent of their liquid capacity (by weight) with distilled water. The remaining 95 percent of the bottle was filled with the solution of interest.

3. The contact time of each bottle was calculated as the difference between the halfway point of the filling of the bottle and the halfway point of the filtration step.

APPENDIX B5

STUDY OF LOSSES

As a result of some suspected losses of TCEA in the initial adsorption isotherms, some studies were conducted in order to verify this. The principal suspected mechanisms were volatization, and adsorption onto the glass.

B5.1 VOLATIZATION STUDY

This study attempted to assess the importance of volatization by analyzing the losses as a function of concentration. The higher the concentration, the bigger was the expected loss. Table B5.1 presents the results of this study.

TABLE B5.1 Volatization Study

INITIAL CONC.	FINAL CONC.	PERCENT REDUCTION
12.0	11.25	7.80
57.3	57.1	0.35
109.5	108.1	1.30
278.0	270.1	8.90
533.0	522.0	2.10

Considering that the standard deviation of the measurements is approximately 5 percent, the observed reductions are insignificant. In

addition, the apparent losses do not seem to be dependent on the concentration.

Long after the completion of the experiment, I was finally able to obtain the value of Henry's Law Constant for this compound. This value was fairly low compared to other similar compounds. The ensuing calculations predicted a volatization loss of 0.02% of the liquid concentration. Thus the observed losses are probably caused by another mechanism.

B5.2 KINETICS OF CONTROLS

The aim of this experiment was to determine if the losses were the result of a diffusion controlled process, such as diffusion through the glass bottle or the cap. The results of this study are shown in Table B5.2. As may be observed, the variation within individual bottles is large. The average loss after 14 days was about 2%, while the analytical error was in the order of 5%. Thus the losses do not appear to be significant, and it is unlikely that diffusional processes are important. The study also compared initial samples taken before and after the kinetic bottles were filled, and a small difference was observed. In addition, this experiment checked if the filtration step was the cause of the losses, but these tests showed that the loss was smaller than the error in the measurement and thus not significant.

It should be noted that the initial samples were taken directly from the reservoir and were not in contact with the adsorption bottles. Thus, the small differences observed in Table B5.2 also include those caused by adsorption onto the glass. The contribution of this mechanism is probably small. Since adsorption is thought to occur almost instantaneously, as a precaution the isotherm bottles were rinsed twice

TABLE B5.2 Kinetics of Controls

COMMENTS	TCEA CONC. (µg/ℓ)	AVERAGE TCEA CONC.	AVERAGE TCEA CONC.	TIME (days)
Samples from the reservoir after the kinetic bottles were filled. (filtered)	567 477	522		
Samples from the reservoir before the kinetic bottles were filled. (filtered)	559 531	559	533	0
Samples from the reservoir before the kinetic bottles were filled. (unfiltered)	526 545	538		
	518	518	518	1
	615	615	615	3
	523	523	523	6
	495	495	495	11
	471 507 537 573		522	14

with the solution before use.

Based on these results, it was concluded that the losses were not significant and that the experimental procedure did not require major changes. The following changes were implemented.

i) Overnight mixing of the isotherm solutions was utilized in an attempt to minimize the apparent variation between the different samples.

ii) At least two and generally three control bottles were used in each experiment and their concentrations were then averaged. These concentrations were used as the initial concentration for the isotherm and kinetic experiments.

APPENDIX CI

1,1,2-TRICHLOROETHANE ADSORPTION ISOTHERM DATA

M/V ADSORPTION (G/L)	C ADSORPTION (MG/L)	Q ADSORPTION (MG/G)	C INITIAL (MG/L)	NN
2.7198	.00023	.1580	.430	1
2.6994	.00027	.1590	.430	2
1.7085	.00039	.2510	.430	3
1.0434	.00153	.4100	.430	4
.6313	.00245	.6000	.430	5
.3589	.00656	1.1780	.430	6
.2385	.01059	1.7560	.430	7
.1355	.01621	2.6920	.430	8
.1122	.03010	3.5580	.430	9
.0972	.03866	3.5190	.430	10
.0986	.03146	3.5440	.430	11
.0659	.06610	4.7830	.430	12
.0448	.10855	6.0830	.430	13
2.6698	.00955	1.5730	4.210	14
1.9446	.01680	2.1560	4.210	15
1.5634	.02805	2.6750	4.210	16
1.0912	.04115	3.8180	4.210	17
.9783	.04580	4.2550	4.210	18
.7912	.07870	5.3200	4.210	19
.6016	.11320	6.8020	4.210	20
.5872	.12650	6.9530	4.210	21
.4745	.15950	8.5340	4.210	22
.4048	.20630	9.8910	4.210	23
.3610	.25000	10.9700	4.210	24
.2462	.43650	15.3270	4.210	25
.2057	.60100	17.5450	4.210	26
.2077	.01600	2.4370	.522	27
.2594	.01100	1.9710	.522	28
.3031	.00850	1.6940	.522	29
.3428	.00740	1.5020	.522	30
.6661	.14000	8.4630	5.777	31
.3116	.42600	17.1200	5.777	32
.2549	.56600	20.5280	5.777	33
.2141	.78300	33.1600	5.777	34
.7661	.24200	11.5600	9.094	35
.7650	.24200	11.5700	9.094	36
.7435	.24500	11.9000	9.094	37
.5987	.36700	14.5800	9.094	38
.5962	.37400	14.2300	9.094	39
.5776	.40300	15.0500	9.094	40
.5722	.39300	15.2100	9.094	41
.4305	.73900	19.4100	9.094	42
.3704	.90300	22.1000	9.094	43
.3102	1.18200	25.5100	9.094	44
.2755	1.43000	27.8200	9.094	45
.2658	1.48600	28.6400	9.094	46
.2496	1.73000	32.0700	9.094	47
.2329	1.77800	31.4700	9.094	48
.2187	1.84300	33.1600	9.094	49

APPENDIX C2

FAUQUIER RIVER WATER ADSORPTION ISOTHERM DATA

C2.1 DILUTED FAUQUIER RIVER WATER ISOTHERM (SUMMER 1982)

M/V ADSORPTION (G/L)	C ADSORPTION (MG/L)	Q ADSORPTION (MG/G)	C INITIAL (MG/L)	NN
.04614	1.382	44.15	3.439	1
.00392	3.174	62.29	3.439	2
.07295	.845	35.3	3.439	3
.05242	1.225	41.85	3.439	4
.12451	.513	23.3	3.439	5
.22293	.293	14.2	3.439	6
.69360	.167	4.75	3.439	8
.67316	.162	4.9	3.439	9
1.43651	.159	2.3	3.439	10
2.99881	.145	1.10	3.439	11
.01167	2.767	59.3	3.439	12
.04016	1.660	44.8	3.439	15
.005911	3.093	62.0	3.439	21

C2.2 FAUQUIER RIVER WATER ISOTHERM (AUGUST 1982)

M/V SORPTION (G/L)	C ADSORPTION (MG/L)	Q ADSORPTION (MG/G)	C INITIAL (MG/L)	NN
.0057	11.58800	114.3300	12.266	1
.0131	10.85500	107.3000	12.266	2
.0282	9.29400	105.3000	12.266	3
.0290	9.27200	103.3000	12.266	4
.0464	7.73200	97.7000	12.266	5
.0601	6.78500	91.2000	12.266	6
.0660	6.72000	84.1000	12.266	7
.1071	4.48000	72.7000	12.266	8
.1302	3.94200	63.9000	12.266	9
.1890	2.56300	50.5000	12.266	10
.1922	2.54200	50.6000	12.266	11
.3337	1.76600	31.4000	12.266	12
.5204	1.14700	21.0000	12.266	13
1.3343	.25800	8.8100	12.266	14
1.3692	.23800	8.6500	12.266	15
1.7770	1.28180	6.1100	12.266	16
3.4768	.15400	3.4300	12.266	17

C2.3 FAUQUIER RIVER WATER ISOTHERM (OCTOBER 1983)

M/V OSORPTION (G/L)	C ADSORPTION (MG/L)	Q ADSORPTION (MG/G)	C INITIAL (MG/L)	NN
2.4638	.083	4.2000	10.368	1
1.8793	.056	5.9000	10.368	2
1.1879	.088	8.9000	10.368	3
.6224	.130	16.4000	10.368	4
.3669	.306	27.3000	10.368	5
.2816	.620	34.5000	10.368	6
.1940	1.268	46.9000	10.368	7
.1583	1.553	55.7000	10.368	8
.1153	2.273	70.2000	10.368	9
.0750	3.843	87.0000	10.368	10
.0687	4.234	89.2000	10.368	11
.0678	4.301	89.5000	10.368	12
.0625	4.704	90.6000	10.368	13
.0629	4.519	93.1000	10.368	14
.0573	4.955	94.4000	10.368	15
.0455	5.893	98.4000	10.368	16
.0358	6.648	103.9000	10.368	17
.0331	6.882	105.3000	10.368	18
.0260	7.637	104.9000	10.368	19
.0247	7.653	110.0000	10.368	20
.0162	8.609	108.8000	10.368	21
.0107	9.178	111.0000	10.368	22

C2.4 FAUQUIER RIVER WATER ISOTHERM (NOVEMBER-DECEMBER 1984)

M/V OSORPTION (G/L)	C ADSORPTION (MG/L)	Q ADSORPTION (MG/G)	C INITIAL (MG/L)	NN
1.8629	.039	4.9000	9.180	1
.2082	1.390	37.4000	9.180	10
.2053	1.440	37.7000	9.180	2
.1335	1.773	55.5000	9.180	3
.0972	2.123	72.6000	9.180	4
.0873	2.389	77.8000	9.180	11
.0744	2.656	87.7000	9.180	5
.0614	3.222	97.1000	9.180	6
.0418	4.555	110.5000	9.180	7
.0361	5.022	115.3000	9.180	8
.0196	6.821	120.5000	9.180	12
.0170	7.197	116.9000	9.180	9

APPENDIX C3

1,1,2-TRICHLOROETHANE DESORPTION ISOTHERM DATA

C3.1 TRICHLOROETHANE DESORPTION ISOTHERM #1

V ADSORPTION (ML)	C ADSORPTION (MG/L)	Q ADSORPTION (MG/G)	C DESORPTION (MG/L)	Q DESORPTION (MG/G)	V DESORPTION (ML)	M (G)
1036.2	108.6	6.083	0.0763	6.083	1028.2	0.04641
1028.9	66.1	4.783	0.0508	4.783	1020.5	0.06775
1040.5	31.5	3.544	0.0292	3.454	1024.9	0.10261
1036.0	38.7	3.519	0.0370	3.809	1036.0	0.10076
347.1	30.1	3.558	0.0377	3.558	347.6	0.03893
1036.4	16.2	2.692	0.0222	2.692	1033.0	0.14042
351.5	10.7	1.756	0.0071	1.185	512.5	0.08383
353.5	6.56	1.178	0.0000	0.000	0.0	0.12688
350.8	2.45	0.600	0.00346	0.600	344.5	0.22147
347.5	1.53	0.410	0.00158	0.420	354.3	0.36257
352.5	0.39	0.251	0.00099	0.251	346.6	0.60224
350.6	0.27	0.159	0.00025	0.159	344.4	0.9464
347.7	0.23	0.158	0.00024	0.158	342.8	0.94564

C3.2 TRICHLOROETHANE DESORPTION ISOTHERM #2

V ADSORPTION (ML)	C ADSORPTION (MG/L)	Q ADSORPTION (MG/G)	C DESORPTION (MG/L)	Q DESORPTION (MG/G)	V DESORPTION (ML)	M (G)
532.500	.0095	1.5732	.0118	1.5699	533.000	1.42168
516.400	.0168	2.1563	.0197	2.1465	534.000	1.00419
544.800	.0281	2.6750	.0264	2.6590	532.500	.80482
533.200	.0412	3.8180	.0503	3.7730	535.500	.58216
513.200	.0458	4.2550	.0640	4.1880	533.500	.50227
542.000	.0797	5.3600	.0845	5.2142	532.700	.40569
513.900	.1192	6.8020	.1245	6.5920	532.800	.31319
533.300	.1265	6.9530	.1328	6.7260	533.900	.30906
540.000	.1595	8.5340	.1891	8.4256	532.400	.24485
516.800	.2063	9.8910	.2265	9.3216	528.900	.20920
517.600	.2500	10.9700	.2516	10.2534	534.500	.19684
532.000	.4165	15.3270	.4216	13.6150	533.000	.13095
518.400	.6010	17.5449	.5086	15.0050	533.900	.10664

C3.3 TRICHLOROETHANE DESORPTION ISOTHERM #3

V ADSORPTION (ML)	C ADSORPTION (MG/L)	Q ADSORPTION (MG/G)	C DESORPTION (MG/L)	Q DESORPTION (MG/G)	V DESORPTION (ML)	M (G)
514.8	0.242	11.560	0.000	0.000	0.0	0.39439
517.8	0.242	11.570	0.246	11.238	539.2	0.39614
512.1	0.239	11.740	0.244	11.405	534.4	0.39608
532.9	0.245	11.900	0.257	11.556	534.0	0.39620
517.4	0.367	14.580	0.363	13.952	537.2	0.30974
517.7	0.374	14.230	0.352	13.623	535.3	0.30865
544.5	0.403	15.050	0.367	14.418	534.6	0.30870
536.9	0.393	15.210	0.340	14.628	532.3	0.30722

APPENDIX C4

FAUQUIER RIVER WATER DESORPTION ISOTHERM DATA

V ADSORPTION (ML)	C ADSORPTION (MG/L)	Q ADSORPTION (MG/G)	C DESORPTION (MG/L)	Q DESORPTION (MG/G)	V DESORPTION (ML)	M (G)
991.1	11.5880	114.330	.2340	94.400	482.5	.00568
990.9	10.6550	107.300	.4170	91.000	509.9	.01303
988.1	9.2340	105.300	.6140	94.000	518.9	.02318
986.6	9.2720	103.300	.7540	89.400	527.3	.02959
991.8	7.7320	97.700	.9020	87.700	512.7	.04602
982.0	6.7850	91.200	.8670	83.800	500.5	.05902
340.4	6.7200	84.100	0.0000	0.000	338.0	.02179
332.5	4.4800	72.700	.6270	66.900	327.9	.03562
321.2	3.9420	63.900	0.0000	0.000	329.1	.04182
336.7	2.5630	50.500	.4990	47.900	346.5	.06363
340.0	2.5420	50.600	.4910	48.000	349.2	.06537
334.6	1.7980	41.400	.3100	30.500	334.1	.11166
331.3	1.1470	21.000	.2010	20.600	336.9	.17240
333.1	.2580	8.810	.0980	8.730	346.6	.44450
33:.9	.2180	8.650	.0970	8.580	329.3	.45450
339.7	1.2018	6.120	.1030	6.050	346.5	.60363
332.2	.1540	3.430	.0680	3.410	344.6	1.15514

APPENDIX D1

BISOLUTE ADSORPTION ISOTHERM DATA

D1.1 COMPETITIVE ISOTHERM #1 (M1)

EXPERIMENT # COMPETITIVE ISOTHERM NO. 1

COMPONENT # 1 = FAUQUIER RIVER WATER

COMPONENT # 2 = TRICHLOROETHANE

INITIAL CONCENTRATION OF COMPOUND # 1 = .100440E+02 MILLIGRAM / L
INITIAL CONCENTRATION OF COMPOUND # 2 = .204900E+01 MILLIGRAM / L

C-1 MILLIG/L	C-2 MILLIG/L	Q-1 MILLIG/G	Q-2 MILLIG/G	V/M LITERS/G
.758500E+01	.176090E+01	.963000E+02	.112850E+02	.391771E+02
.449400E+01	.112130E+01	.810000E+02	.135430E+02	.145986E+02
.237400E+01	.714200E+00	.679000E+02	.118170E+02	.885301E+01
.239000E+01	.634500E+00	.682000E+02	.126110E+02	.888252E+01
.142600E+01	.315400E+00	.461000E+02	.926600E+01	.535686E+01
.793000E+00	.194700E+00	.366900E+02	.734600E+01	.396128E+01
.313300E+00	.896000E-01	.253300E+02	.509500E+01	.260023E+01
.112500E+00	.301000E-01	.164800E+02	.333200E+01	.165771E+01
.956000E-01	.161000E-01	.106400E+02	.217200E+01	.106859E+01
.570000E-01	.820000E-02	.698000E+01	.140800E+01	.689830E+00
.530000E-01	.290000E-02	.409500E+01	.831800E+00	.489434E+00
.107000E+00	.141000E-02	.212500E+01	.437000E+00	.213637E+00

D1.2 REPEAT OF COMPETITIVE ISOTHERM #1 (MIB)

EXPERIMENT # COMPETITIVE ISOTHERM NO. 1

COMPONENT # 1 = FAUQUIER RIVER WATER

COMPONENT # 2 = TRICHLOROETHANE

INITIAL CONCENTRATION OF COMPUND # 1 = .100440E+02 MILLIGRAM / L
INITIAL CONCENTRATION OF COMPOUND # 2 = .204900E+01 MILLIGRAM / L

C-1 MILLIG/L	C-2 MILLIG/L	Q-1 MILLIG/G	Q-2 MILLIG/G	V/M LITERS/G
.766000E+01	.167800E+01	.103400E+03	.181240E+02	.491115E+02
.687600E+01	.163740E+01	.995000E+02	.141050E+02	.344337E+02
.672200E+01	.160100E+01	.999000E+02	.120080E+02	.328037E+02
.532400E+01	.131600E+01	.940000E+02	.151250E+02	.206899E+02
.514400E+01	.126500E+01	.911000E+02	.155715E+02	.199109E+02
.483000E+01	.119600E+01	.873000E+02	.150540E+02	.176890E+02
.471900E+01	.121900E+01	.871000E+02	.142690E+02	.172330E+02
.335200E+01	.930000E+00	.829000E+02	.144310E+02	.129192E+02
.329500E+01	.847000E+00	.741000E+02	.137380E+02	.114484E+02
.305700E+01	.829000E+00	.746500E+02	.135540E+02	.111287E+02
.242500E+01	.726000E+00	.684000E+02	.123060E+02	.931556E+01
.105300E+01	.268700E+00	.435000E+02	.888800E+01	.499813E+01
.800000E-01	.185000E-01	.102800E+02	.212900E+01	.104929E+01

D1.3 COMPETITIVE ISOTHERM #2 (M2)

EXPERIMENT # COMPETITIVE ISOTHERM NO. 2

COMPONENT # 1 = FAUQUIER RIVER WATER

COMPONENT # 2 = TRICHLOROETHANE

INITIAL CONCENTRATION OF COMPUND # 1 = .989700E+01 MILLIGRAM / L
INITIAL CONCENTRATION OF COMPOUND # 2 = .349800E+00 MILLIGRAM / L

C-1 MILLIG/L	C-2 MILLIG/L	Q-1 MILLIG/G	Q-2 MILLIG/G	V/M LITERS/G
.724400E+01	.257100E+00	.100000E+03	.337700E+01	.376829E+02
.561000E+01	.189700E+00	.961200E+02	.359000E+01	.226665E+02
.539200E+01	.185800E+00	.927000E+02	.337700E+01	.205934E+02
.369600E+01	.106900E+00	.835000E+02	.323100E+01	.134610E+02
.249800E+01	.582000E-01	.723900E+02	.285800E+01	.978438E+01
.165800E+01	.306000E-01	.531100E+02	.205800E+01	.644639E+01
.579300E+00	.186000E-01	.335000E+02	.119100E+01	.359454E+01
.323000E+00	.149000E-01	.278000E+02	.970000E+00	.289536E+01
.950000E-01	.800000E-02	.172000E+02	.600000E+00	.146519E+01
.430000E-01	.130000E-02	.890000E+01	.315000E+00	.904838E+00
.310000E-01	.490000E-03	.430000E+01	.156000E+00	.445077E+00

D1.4 COMPETITIVE ISOTHERM #3 (M3)

EXPERIMENT # COMPETITIVE ISOTHERM NO. 3

COMPONENT # 1 = FAUQUIER RIVER WATER

COMPONENT # 2 = TRICHLORDETHANE

INITIAL CONCENTRATION OF COMPUND # 1 = .345800E+01 MILLIGRAM / L
INITIAL CONCENTRATION OF COMPOUND # 2 = .453100E+00 MILLIGRAM / L

C-1 MILLIG/L	C-2 MILLIG/L	Q-1 MILLIG/G	Q-2 MILLIG/G	V/M LITERS/G
.260300E+01	.424860E+00	.882000E+02	.246850E+01	.874433E+02
.180800E+01	.317500E+00	.635000E+02	.502780E+01	.370765E+02
.194600E+01	.273200E+00	.562900E+02	.643190E+01	.357560E+02
.149000E+01	.261500E+00	.570800E+02	.538660E+01	.281118E+02
.145500E+01	.257000E+00	.580100E+02	.550840E+01	.280872E+02
.120300E+01	.214300E+00	.536000E+02	.552266E+01	.231280E+02
.978000E+00	.177400E+00	.484000E+02	.524840E+01	.190371E+02
.939000E+00	.168400E+00	.475900E+02	.524890E+01	.184377E+02
.616000E+00	.117300E+00	.388400E+02	.449350E+01	.137855E+02
.346000E+00	.751000E-01	.316200E+02	.376570E+01	.996184E+01
.388000E+00	.695000E-01	.297200E+02	.363910E+01	.948756E+01
.211000E+00	.237000E-01	.175200E+02	.220670E+01	.513906E+01
.620000E-01	.129000E-01	.119400E+02	.151930E+01	.345156E+01
.438000E-01	.650000E-02	.799000E+01	.102650E+01	.229856E+01
.480000E-01	.155000E-02	.348000E+01	.452700E+00	.977510E+00
.320000E-01	.800000E-03	.194000E+01	.251100E+00	.555146E+00

APPENDIX E1

ERROR ANALYSIS FOR THE ISOTHERMS

As isotherms are generally plotted as equilibrium solid phase concentration q versus equilibrium liquid phase concentration c , it is of interest to calculate the 95% confidence interval of q at different data points. To do so, the variance of q at each point must first be calculated.

E1.1 CALCULATION OF THE VARIANCES OF THE SOLID PHASE CONCENTRATIONS FOR THE ADSORPTION EXPERIMENT

The loading is calculated by

$$q = \frac{(c_o - c) \cdot V}{M} \qquad \text{(E1.1)}$$

where V = liquid volume, ℓ;

M = mass of carbon used, g;

q = equilibrium solid phase concentration, mg solute/g carbon;

c_o = initial liquid phase concentration, mg/ℓ; and,

c = equilibrium liquid phase concentration, mg/ℓ.

And the general formula for the variance is

$$\text{var}(Q) = \sum_{i=1}^{N} \left[\frac{\partial Q}{\partial y_i}\right]^2 \cdot \text{var}(y_i) + 2\sum_{i=1}^{N}\sum_{j=1}^{N} \left(\frac{\partial Q}{\partial y_i}\right)\left(\frac{\partial Q}{\partial y_j}\right) \text{cov}(y_i, y_j) \qquad \text{(E1.2)}$$

where Q = the dependent variable;

y_i = the independent variables used to calculate Q; and,

N = the total number of variables.

Since c_o, c, V and M are measured independently, the covariances are zero.

$$\frac{\partial q}{\partial c_o} = \frac{V}{M} \qquad \text{(E1.3)}$$

$$\frac{\partial q}{\partial c} = \frac{-V}{M} \qquad \text{(E1.4)}$$

$$\frac{\partial q}{\partial V} = \frac{(c_o-c)}{M} \qquad \text{(E1.5)}$$

$$\frac{\partial q}{\partial M} = \frac{(c_o-c)\,V}{M^2} \qquad \text{(E1.6)}$$

$$\text{var}(q) = \left(\frac{V}{M}\right)^2(\sigma_{c_o})^2 + \left(\frac{-V}{M}\right)^2(\sigma_c)^2 + \left(\frac{c_o-c}{M}\right)^2(\sigma_V)^2 + \left(\frac{(c_o-c)V}{M^2}\right)^2(\sigma_M)^2 \qquad \text{(E1.7)}$$

A listing of a computer program that performs the above calculations for all the data points is presented in Appendix E2.

E1.2 CALCULATION OF THE VARIANCES OF THE SOLID PHASE CONCENTRATIONS FOR THE DESORPTION ISOTHERMS

The solid phase concentration after a desorption cycle is calculated by the following mass balance

$$q_{des} = q + \frac{(c_{od}-c_{des}) \cdot V_{des}}{M_{des}} \qquad \text{(E1.8)}$$

where q_{des} = equilibrium solid phase concentration after a desorption cycle, mg solute/g carbon;

q = equilibrium solid phase concentration prior to the desorption cycle, mg solute/g carbon;

c_{o_d} = initial liquid phase concentration for the desorption cycle, mg/ℓ;

c_{des} = liquid phase concentration at the end of the desorption cycle, mg/ℓ;

V_{des} = liquid volume, ℓ; and,

M_{des} = mass of carbon, g.

Since the carbon mass from the adsorption cycle was also used in the desorption cycle, M_{des} equals M. Substituting in equation (E1.1), one obtains

$$q_{des} = \frac{(c_o - c) \cdot V}{M} + \frac{(c_{o_d} - c_{des}) \cdot V_{des}}{M} \qquad \text{(E1.9)}$$

Since c_o, c, V, M, C_{o_d}, c_{des} and V_{des} are measured independently, their covariances are zero. Thus the variance of q_{des} can be calculated using only the first summation term in equation (E1.2). The necessary derivatives are:

$$\frac{\partial q_{des}}{\partial c_o} = \frac{V}{M} \qquad \text{(E1.10)}$$

$$\frac{\partial q_{des}}{\partial c} = \frac{-V}{M} \qquad \text{(E1.11)}$$

$$\frac{\partial q_{des}}{\partial V} = \frac{(c_o - c)}{M} \qquad \text{(E1.12)}$$

$$\frac{\partial q_{des}}{\partial c_{o_d}} = \frac{V_{des}}{M} \qquad \text{(E1.13)}$$

$$\frac{\partial q_{des}}{\partial c_{des}} = \frac{-V}{M} \qquad \text{(E1.14)}$$

$$\frac{\partial q_{des}}{\partial V_{des}} = \frac{(c_{o_d} - c_{des})}{M} \qquad \text{(E1.15)}$$

$$\frac{\partial q_{des}}{\partial M} = \frac{(c_o - c) \cdot V}{M^2} + \frac{(c_{o_d} - c_{des}) \cdot V_{des}}{M^2} \qquad \text{(E1.16)}$$

Substituting equations (E1.10) through (E1.16) into equation (E1.2), one obtains

$$\text{var}(q_{des}) = \left(\frac{V}{M}\right)^2(\sigma_{c_o})^2 + \left(\frac{-V}{M}\right)^2(\sigma_c)^2 + \left(\frac{c_o - c}{M}\right)^2(\sigma_V)^2$$

$$+ \left(\frac{V_{des}}{m}\right)^2(\sigma_{c_{o_d}})^2 + \left(\frac{-V_{des}}{M}\right)^2(\sigma_{cdes})^2 + \left(\frac{c_{o_d} - c_{des}}{M}\right)^2(\sigma_{Vdes})^2$$

$$+ \left(\left(\frac{(c_o - c)V}{M^2}\right)^2 + \left(\frac{(c_{o_d} - c_{des})V_{des}}{M^2}\right) \right)^2(\sigma_M)^2 \qquad \text{(E1.17)}$$

Substituting in Equation E1.7, it reduces to

$$\text{var}(q_{des}) = 1 \cdot \text{var}(q) +$$

$$\left(\frac{V_{des}}{M}\right)^2(\sigma_{c_{o_d}})^2 + \left(\frac{-V_{des}}{M}\right)^2(\sigma_{cdes})^2 + \left(\frac{c_{o_d} - c_{des}}{M}\right)^2(\sigma_{Vdes})^2$$

$$+ \left(\frac{(c_{o_d} - c_{des})V_{des}}{M^2}\right)^2(\sigma_M)^2 \qquad \text{(E1.18)}$$

Appendix E2 provides a computer program listing that can be used to calculate the variances of q_{des} as above.

E1.3 APPLICATION OF THE ERROR ANALYSIS TO THE SECOND 1,1,2-TRICHLOROETHANE ADSORPTION AND DESORPTION ISOTHERMS

In this particular case the estimated values of the standard deviations of the independent variables were:

$\sigma(M) = 0.0002$ g ;

$\sigma(V) = 0.0001$ ℓ ;

$\sigma(c_o) = 0.049 \cdot c_o$;

$\sigma(c) = 0.049 \cdot c$;

$\sigma(V_{des}) = 0.0001$ ℓ ;

$\sigma(c_{o_d}) = 0.049 \cdot c_{o_d}$; and,

$\sigma(c_{des}) = 0.049 \cdot c_{des}$.

The error for TCEA increased at the lower concentrations to about 10%, but the points of interest were at the higher levels where the error was fairly constant.

The variance and the 95% confidence intervals for both the adsorption and the desorption cycles were calculated with the program listed in Appendix E2. The results of these calculations are shown in Tables E1.1 and E1.2, and also in Figure E1.1.

E1.1 Confidence Interval in the Adsorption Isotherm

V ADSORPTION (L)	C ADSORPTION (MG/L)	Q ADSORPTION (MG/G)	Q+95% ADSORPTION (MG/G)	Q-95% ADSORPTION (MG/G)	C ADSORPTION (MG/L)	M (G)
.5325	.0095	1.573	1.728	1.419	.0095	1.42168
.5164	.0168	2.156	2.368	1.944	.0168	1.00419
.5148	.0234	2.675	2.939	2.411	.0234	.80482
.5332	.0412	3.818	4.196	3.440	.0412	.58216
.5132	.0456	4.255	4.677	3.833	.0456	.50227
.5120	.0797	5.320	5.842	4.798	.0787	.40509
.5139	.1192	6.802	7.475	6.125	.1192	.31319
.5333	.1265	6.953	7.665	6.241	.1265	.30906
.5160	.1595	8.534	9.404	7.664	.1595	.24485
.5168	.2063	9.891	10.912	8.870	.2063	.20920
.5176	.2500	10.970	12.115	9.825	.2500	.18684
.5320	.4365	15.327	17.013	13.641	.4365	.13095
.5184	.6010	17.545	19.572	15.518	.6010	.10664

E1.2 Confidence Interval in the Desorption Isotherm

V DESORPTION (L)	C DESORPTION (MG/L)	Q DESORPTION (MG/G)	Q+95% DESORPTION (MG/G)	Q-95% DESORPTION (MG/G)	C DESORPTION (MG/L)	M (G)
.5340	.0118	1.570	1.724	1.415	.0118	1.42168
.5140	.0197	2.147	2.359	1.934	.0197	1.01419
.5325	.0261	2.659	2.923	2.395	.0261	.80482
.5355	.0503	3.773	4.152	3.395	.0503	.58216
.5335	.0640	4.188	4.610	3.766	.0640	.50227
.5327	.0849	5.214	5.736	4.692	.0849	.40509
.5318	.1249	6.592	7.270	5.914	.1249	.31319
.5339	.1328	6.726	7.435	6.013	.1328	.30906
.5324	.1891	8.126	8.997	7.254	.1891	.24485
.5289	.2265	9.322	10.344	8.299	.2265	.20920
.5349	.2516	10.253	11.401	9.106	.2516	.18684
.5330	.4218	13.615	15.309	11.921	.4218	.13095
.5329	.5086	15.005	17.047	12.963	.5086	.10664

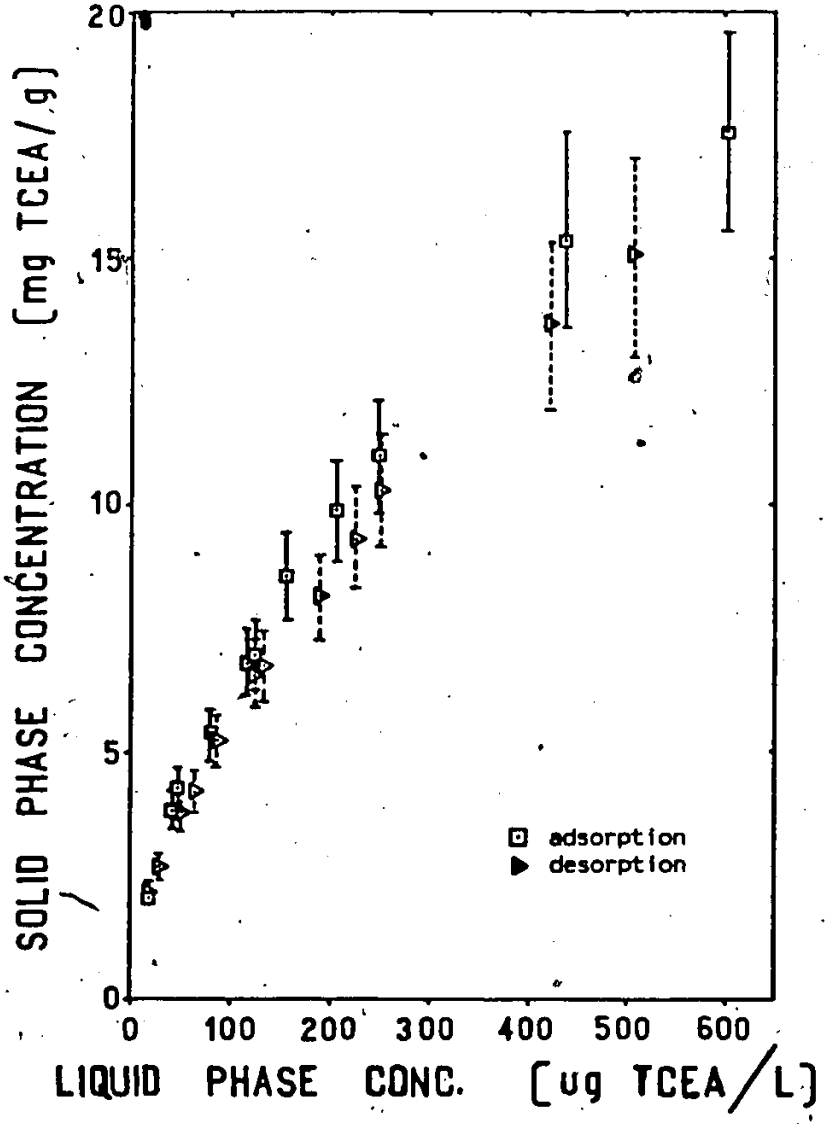

FIGURE E1.1 Trichloroethane Adsorption and Desorption Isotherm #2 with 95% Confidence Interval Bars.

APPENDIX E2

PROGRAM FOR THE CALCULATION OF THE CONFIDENCE INTERVAL OF THE SOLID PHASE CONCENTRATIONS IN ADSORPTION AND DESORPTION ISOTHERMS

```
      PROGRAM ERROR (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      DIMENSION CDES(40),CDESS(40),QDES(40),VADS(40),VDES(40)
      DIMENSION QADS(40),CADS(40),VMEXP(40)
      DIMENSION CQADS(40),CQDES(40),VARCOA(40),VARCOD(40),VARCAD(40),
     1VARCDE(40),VARMEX(40),VARVAD(40),VARVDE(40)
      DIMENSION DC0(40),DCADS(40),DMEXP(40),DVADS(40),DVDES(40),
     1CQDES(40),DCQDES(40)
      DIMENSION VARQAD(40),VARQDE(40),QADHI(40),QADLO(40),QDESHI(40)
     1,QDESLO(40)
      REAL MEXP(40),MEX,C00(40)
      READ(5,*) NPROB,NOB1,NOB,NP,NPTS
      READ(5,*) C01,C02
      NOB1P=NOB+1
      WRITE(6,9210)
      DO 50 I=1,NPTS
      READ(5,*) VAD,CAD,QAD,MEX,VDE,CDE,QDE
      WRITE(6,9000) VAD, CAD, QAD, CDE, QDE, VDE, MEX
   50 CONTINUE
      WRITE(6,9200)
      READ(5,*) (VADS(I),CADS(I),QADS(I),MEXP(I),VDES(I),
     1   CDES(I),QDES(I),I=1,NOB1)
      DO 100 I=1,NOB
      WRITE(6,1050) VADS(I),CADS(I),QADS(I),CDES(I),QDES(I),VDES(I)
     1,MEXP(I)
      VADS(I)=VADS(I)/1000.0
      VDES(I)=VDES(I)/1000.0
      CADS(I)=C01
      CQDES(I)=C02
  100 CONTINUE
      WRITE(6,10) NPROB,NOB,NP,NPTS
   10 FORMAT(1X,"  NPROB = ",I5/" ","     NOB  = ",I2/" ","     NP = "
     1,I2/" ","     NPTS  = ",I3////)
      WRITE(6,9800)
      DO 300 I=1,NOB
      VARCOA(I)=(0.05*CQADS(I))**2
      VARCAD(I)=(0.05*CADS(I))**2
      VARVAD(I)=(0.0001)**2
      VARVDE(I)=(0.0001)**2
      VARMEX(I)=(0.0002)**2
      VARCQD(I)=(0.1*CQDES(I))**2
      VARCDE(I)=(0.05*CDES(I))**2
      DC0(I)=VADS(I)/MEXP(I)
      DCADS(I)=-DC0(I)
      DVADS(I)=(CQADS(I)-CADS(I))/MEXP(I)
      DMEXP(I)=DVADS(I)*DC0(I)
      VARQAD(I)=(DC0(I)**2)*VARCOA(I) + (DCADS(I)**2)*VARCAD(I)
     1          + (DVADS(I)**2)*VARVAD(I) + (DMEXP(I)**2)*VARMEX(I)
      QADHI(I)=QADS(I)+1.96*SQRT(VARQAD(I))
      QADLO(I)=QADS(I)-1.96*SQRT(VARQAD(I))
      PRINT*," I=",I," VARCOA=",VARCOA(I),"  VRCAD(I)=",VARCAD(I),
     1" VARMEX=",VARMEX(I),"  VARVAD=",VARVAD(I)
      PRINT*," C00=",C00(I),"  DC0(I)=",DC0(I),"  DCADS=",DCADS(I),"  DMEXP=",
     1DMEXP(I),"  DVADS=",DVADS(I)
      PRINT*," VARQAD=",VARQAD(I),"  QADHI=",QADHI(I),"  QADLO=",
     1QADLO(I)
  300 CONTINUE
      WRITE(6,9888)
```

```
      WRITE(6,9210)
      DO 350 I=1,NOB
      WRITE(6,9010) VADS(I),CADS(I),QADS(I),QADHI(I),
     1QADLO(I),CADS(I),MEXP(I)
  350 CONTINUE
      WRITE(6,9900)
      DO 400 I=1,NOB
      DCODES(I)=VDES(I)/MEXP(I)
      DCDES(I)=-VDES(I)/MEXP(I)
      DVDES(I)=(CODES(I)-CDES(I))/MEXP(I)
      DMEXP(I)=(CODES(I)-CDES(I))*VDES(I)/(MEXP(I)**2)
      VARQDE(I) = VARQAD(I) + ((DCODES(I)**2)*VARCOD(I))
     1                      + ((DCDES(I)**2)*VARCDE(I))
     1                      + ((DVDES(I)**2)*VARVDE(I))
     1                      + ((DMEXP(I)**2)*VARMEX(I))
      QDESHI(I)=QDES(I)+1.96*SQRT(VARQDE(I))
      QDESLO(I)=QDES(I)-1.96*SQRT(VARQDE(I))
      PRINT*,"I=",I," VARQAD=",VARQAD(I)," VARCOD=",VARCOD(I),
     1" VARCDE=",VARCDE(I)," VARMEX=",VARMEX(I)," VARVDE=",VARVDE(I)
      PRINT*,"             DCODES=",DCODES(I)," DCDES=",DCDES(I)," DMEXP=",
     1DMEXP(I)," DVDES=",DVDES(I)
      PRINT*,"             VARQDE=",VARQDE(I)," QDESHI=",QDESHI(I),
     1" QDESLO=",QDESLO(I)
  400 CONTINUE
      WRITE(6,9900)
      WRITE(6,9220)
      DO 450 I=1,NOB
      WRITE(6,9010) VDES(I),CDES(I),QDES(I),QDESHI(I),
     1QDESLO(I),CDES(I),MEXP(I)
  450 CONTINUE
 9100 FORMAT(" ",F8.4,1X,F8.3,1X,F8.4,1X,F8.3,1X,F9.4,1X,F8.3)
 9000 FORMAT(" ",2X,F5.1,5X,F8.4,3X,F8.3,2X,F8.4,3X,F8.3,2X,F5.1,
     1      5X,F8.2)
 9010 FORMAT(" ",1X,F6.4,4X,F7.4,3X,F8.3,3X,F8.3,3X,F8.3,4X,F7.4,
     1      3X,F8.5)
 9050 FORMAT(" ",F8.3,3X,F8.4,4X,F8.4,1X,F8.4,3X,F8.4,3X,F8.3,3X,
     1F8.5)
 9200 FORMAT("1","           V              C               Q              C      ",
     1          "           Q                                    M     "/
     2          " ","ADSORPTION ADSORPTION ADSORPTION DESORPTION ",
     3          "DESORPTION DESORPTION                    "/
     4          " ","   (ML)         (MG/L)        (MG/G)        (MG/L)      ",
     5          "   (MG/G)        (M_)           (G)      "/)
 9210 FORMAT("-","           V              C               Q            Q+95%   ",
     1          "        Q-95%           C                M     "/
     2          " ","ADSORPTION ADSORPTION ADSORPTION ADSORPTION ",
     3          "ADSORPTION ADSORPTION                    "/
     4          " ","    (L)         (MG/_)        (MG/G)        (MG/G)     ",
     5          "   (MG/G)        (MG/L)           (G)      "/)
 9220 FORMAT("-","           V              C               Q            Q+95%   ",
     1          "        Q-95%           C                M     "/
     2          " ","DESORPTION DESORPTION DESORPTION DESORPTION ",
     3          "DESORPTION DESORPTION                    "/
     4          " ","    (L)         (MG/L)        (MG/G)        (MG/G)     ",
     5          "   (MG/G)        (MG/L)           (G)      "/)
 9800 FORMAT("1",26X,"ERROR IN THE ADSORPTION ISOTHERM"////)
 9900 FORMAT("1",20X,"ERROR IN THE DESORPTION ISOTHERM"///)

      STOP
      END
```

APPENDIX F1

APPLICATION OF ORTHOGONAL COLLOCATION TO THE SOLUTION OF THE BATCH KINETICS EQUATIONS

The equations describing the batch kinetics problem are

$$\frac{dC}{d\theta} = F1 \cdot BIF \cdot (C-C_s) \tag{5.15}$$

$$\frac{\partial Q_m}{\partial \theta} = \frac{1}{\beta^2}\frac{\partial}{\partial \beta}\left(\beta^2 \frac{\partial Q_m}{\partial \beta}\right) - \frac{BIP}{f}(Q_m-Q_b) \tag{5.16}$$

$$\frac{\partial Q_b}{\partial \theta} = \frac{BIF}{(1-f)} \cdot (Q_m-Q_b) \tag{5.17}$$

$$\left.\frac{\partial Q_m}{\partial \beta}\right|_{\beta=1} = \frac{BIF \cdot BIGF}{3 \cdot f}(C-C_s) \tag{5.18}$$

Collocation methods approximate the solution of a differential equation by a trial function which has its coefficients adjusted so that the function gives an exact solution at the collocation points. Orthogonal collocation, developed by Villadsen and Stewart (1967), uses a set of orthogonal polynomials as the trial function and the roots of the polynomials are the collocation points. Villadsen and Stewart (1967) calculated the roots of these polynomials as well as the coefficients of the trial function and their spatial derivatives for several geometries. The replacement of the spatial derivatives in the equations being solved by the corresponding matrices reduces the

dimensions of the differential equations by one. Thus the PDEs 5.15 to 5.18 are reduced to a set of ordinary differential equations with respect to time, so this becomes an initial value problem. A further advantage of the polynomials used by Villadsen and Stewart (1967) is that due to their being in terms of $(1-x)^2$, they automatically satisfy symmetry conditions such as the central boundary conditions of the carbon particle (equation 5.26).

Orthogonal collocation was applied following the procedure outlined by Villadsen and Stewart (1967). In orthogonal collocation, the gradient and Laplacian operators for function $g(\beta)$ are represented by

$$\left.\frac{\partial g}{\partial \beta}\right|_{\beta=\beta_i} = \sum_{j=1}^{N+1} A_{ij} \cdot g(\beta_j) \qquad \text{(F1.1)}$$

$$\left.\frac{1}{\beta^2}\frac{\partial}{\partial \beta}\left(\beta^2 \frac{\partial g}{\partial \beta}\right)\right|_{\beta=\beta_i} = \sum_{j=1}^{N+1} B_{ij} \cdot g(\beta_j) \qquad \text{(F1.2)}$$

where β_i = the collocation points;

N = number of internal collocation points;

$N+1$ = index of the boundary collocation point;

A_{ij} = coefficient of the first derivative approximation;

B_{ij} = coefficient of the Laplacian approximation.

And the above authors also provided formulas for volume averaging of different geometries. For spherical geometry

$$\int_0^1 \beta^2 \cdot g(\beta)\, d\beta = \sum_{i=1}^{N+1} W_i \cdot g(\beta_i) \qquad \text{(F1.3)}$$

The values of the collocation points β_i and the coefficients of the matrices A, B and W are listed for cases of up to three collocation points. Villadsen and Michelsen (1978) presented listings of programs

that calculate the values of these coefficients for any number of collocation points. This reference also presents programs to calculate the coefficients for several other weighted residuals methods, of which orthogonal collocation is a particular application.

F1.1 APPLICATION OF ORTHOGONAL COLLOCATION TO EQUATIONS 5.16, 5.17 AND 5.15

i) Macropore Balance (equation 5.16) applying equation F1.2 becomes

$$\left.\frac{\partial Q_m}{\partial \theta}\right|_{\beta=\beta_i} = \sum_{j=1}^{N+1} B_{ij} \cdot Q_m(\beta_i) - \frac{BIP}{f}(Q_m(\beta_i)-Q_b(\beta_i)) \qquad (F1.4)$$

ii) Micropore Balance (equation 5.17)

$$\left.\frac{\partial Q_b}{\partial \theta}\right|_{\beta=\beta_i} = \frac{BIP}{(1-f)}(Q_m(\beta_i)-Q_b(\beta_i)) \qquad (F1.5)$$

iii) Liquid Volume Balance (equation 5.15)

$$\frac{dC}{d\theta} = F1 \cdot BIF \cdot (C-C_s) \qquad (F1.6)$$

F1.2 HANDLING OF THE LIQUID PHASE - SOLID PHASE BOUNDARY CONDITION

i) First use the Macropore Balance

$$\frac{\partial Q_m}{\partial \theta} = \frac{1}{\beta^2}\frac{\partial}{\partial \beta}\left(\beta^2 \frac{\partial Q_m}{\partial \beta}\right) - \frac{BIP}{f}(Q_m-Q_b) \qquad (5.16)$$

ii) Averaging a function f(x) over the volume of a spherical particle is

$$\bar{f(x)} = \frac{4\pi \int_0^1 \beta_2^2 \cdot f(\beta)\, d\beta}{\frac{4\pi}{3}(1)^3} = 3\int_0^1 \beta_2^2 \cdot f(\beta)\, d\beta \qquad (F1.7)$$

iii) Then averaging over volume equation 5.16

$$3\int_0^1 \beta^2 \frac{\partial Q_m}{\partial \theta}\, d\beta = 3\int_0^1 \beta^2 \frac{1}{\beta^2}\frac{\partial}{\partial \beta}\left(\beta^2 \frac{\partial Q_m}{\partial \beta}\right) d\beta - \frac{BIP}{f} \cdot 3\int_0^1 \beta^2 (Q_m-Q_b)\, d\beta \qquad (F1.8)$$

$$\int_0^1 \beta^2 \frac{\partial Q_m}{\partial \theta}\, d\beta = \beta^2 \frac{\partial Q_m}{\partial \beta}\Bigg|_0^1 - \frac{BIP}{f} \int_0^1 \beta^2 (Q_m - Q_b)\, d\beta \qquad (F1.9)$$

$$\int_0^1 \beta^2 \frac{\partial Q_m}{\partial \theta}\, d\beta = \left(1 \cdot \frac{\partial Q_m}{\partial \beta}\Bigg|_{\beta=1} - 0.0\right) - \frac{BIP}{f} \int_0^1 \beta^2 (Q_m - Q_b)\, d\beta \qquad (F1.10)$$

iv) In a general form the collocation version of volume averaging $f(\beta)$ is

$$\bar{f}(\beta) = 3\int_0^1 \beta^2 \cdot f(\beta)\, d\beta = 3 \sum_{j=1}^{N+1} W_j \cdot f(\beta_j) \qquad (F1.11)$$

thus

$$\int_0^1 \beta^2 \frac{\partial Q_m}{\partial \theta}\, d\beta = \sum_{j=1}^{N+1} W_j \cdot \left(\frac{\partial Q_{m_j}}{\partial \theta}\right) \qquad (F1.12)$$

$$\int_0^1 \beta^2 (Q_m - Q_b)\, d\beta = \sum_{j=1}^{N+1} W_j \cdot (Q_{m_j} - Q_{b_j}) \qquad (F1.13)$$

v) Applying F1.12 and F1.13 to equation F1.10 becomes

$$\sum_{j=1}^{N+1} W_j \left(\frac{\partial Q_{m_j}}{\partial \theta}\right) = \frac{\partial Q_m}{\partial \beta}\Bigg|_{\beta=1} - \frac{BIP}{f} \sum_{j=1}^{N+1} W_j (Q_{m_j} - Q_{b_j}) \qquad (F1.14)$$

vi) The boundary condition equation between the liquid phase and the solid phase (equation 5.18) is

$$\frac{\partial Q_m}{\partial \beta}\Bigg|_{\beta=1} = \frac{\overline{BIF} \cdot BIGF}{3 \cdot f} (C - C_s) \qquad (5.18)$$

which when substituted into equation F1.14 gives

$$\sum_{j=1}^{N+1} W_j \left(\frac{\partial Q_{m_j}}{\partial \theta}\right) = \frac{BIF \cdot BIGF}{3 \cdot f} (C - C_s) - \frac{BIP}{f} \cdot \sum_{j=1}^{N+1} W_j (Q_{m_j} - Q_{b_j}) \qquad (F1.15)$$

which can be rearranged to

$$\frac{\partial Q_m}{\partial \theta}\Bigg|_{\beta=\beta_{N+1}} = \frac{BIF \cdot BIGF}{3 \cdot f \cdot W_{N+1}} (C - C_s) - \frac{BIP}{f} \frac{1}{W_{N+1}} \sum_{j=1}^{N+1} W_j (Q_{m_j} - Q_{b_j}) - \frac{1}{W_{N+1}} \sum_{j=1}^{N} W_j \left(\frac{\partial Q_{m_j}}{\partial \theta}\right) \qquad (F1.16)$$

F1.3 SUMMARY

Thus one must solve simultaneously the ordinary differential equations that describe the batch kinetics test for each elapsed time. These equations, which were derived above, are as follows:

$$\frac{dC}{d\theta} = F1 \cdot BIF \cdot (C-C_s) \qquad (5.15)$$

$$\left.\frac{\partial Q_b}{\partial \theta}\right|_{\beta=\beta_i} = \frac{BIP}{(1-f)}(Q_m(\beta_i)-Q_b(\beta_i)) \qquad \text{for } i = 1 \text{ to } N+1 \qquad (F1.5)$$

$$\left.\frac{\partial Q_m}{\partial \theta}\right|_{\beta=\beta_i} = \sum_{j=1}^{N+1} B_{ij}Q_m(\beta_i) - \frac{BIP}{f}(Q_m(\beta_i)-Q_b(\beta_i)) \qquad \text{for } i = 1 \text{ to } N \qquad (F1.4)$$

$$\left.\frac{\partial Q_m}{\partial \theta}\right|_{\beta=\beta_{N+1}} = \frac{BIF \cdot BIGF}{3 \cdot f \cdot W_{N+1}}(C-C_s) - \frac{BIP}{f}\frac{1}{W_{N+1}}\sum_{j=1}^{N+1} W_j(Q_{m_j}-Q_{b_j}) - \frac{1}{W_{N+1}}\sum_{j=1}^{N} W_j\left(\frac{\partial Q_{m_j}}{\partial \theta}\right) \qquad \text{for } i = N+1 \qquad (F1.16)$$

These equations have to be solved by a numerical technique such as Runge-Kutta. In this case it will be solved using the IMSL (1982) routine DGEAR based on the GEAR method. A listing of the program used to simulate the single component batch kinetics test is presented in Appendix F3. And Appendix F2 presents confirmation of the suitability of the collocation technique by a comparison with published data.

APPENDIX F2

PREDICTION BY THE PROGRAM SEAR5 FOR THE PHENOL DATA OF PEEL (1980)

To verify that the orthogonal collocation technique could solve the dual rate model proposed by Peel (1980), the program developed in this study was used to simulate the Phenol IV Run data from Peel's thesis. Peel (1980) developed a program which solved his dual rate model using Crank-Nicholson finite difference operators. Since the program developed by Peel was not readily available, direct comparison between the values of the concentrations yielded by the two solution techniques was not possible. Instead, the parameters obtained by Peel were used in the collocation based computer program called SEAR5 (Appendix F3) to simulate the data. The results of this simulation (Table F2.1) were plotted in the same size graph as that in Peel's thesis for the same data (Figure F2.1). Tracing Peel's simulation onto Figure F2.1 showed a complete overlap. Thus, the program SEAR5 and the collocation technique provide a suitable solution to Peel's dual rate model.

TABLE F2.1 Simulation of the Phenol Run No. IV from Peel (1980) by the Program SEAR5 which Utilizes the Orthogonal Collocation Method.

I	MINUTES	CONCENTRATION (MICROG/L)	REDUCED CONCEN.	PREDICTED	TIME (SEC.)
1	.5	94.900000	.992678	.994315	30.0
2	1.0	94.500000	.988494	.988663	60.0
3	1.5	94.000000	.983284	.983044	90.0
4	2.0	93.500000	.978033	.977463	120.0
5	3.0	92.500000	.967573	.966438	180.0
6	6.0	89.500000	.936192	.935135	360.0
7	10.0	86.100000	.900628	.899260	600.0
8	30.0	74.800000	.782427	.783328	1810.0
9	60.0	66.000000	.690377	.694493	3600.0
10	122.0	58.500000	.611925	.611822	7320.0
11	190.0	55.300000	.578452	.574824	11400.0
12	295.0	53.200000	.556485	.553601	17710.0
13	397.0	52.300000	.547071	.545215	23820.0
14	670.0	50.300000	.526151	.532199	40230.0
15	1000.0	49.200000	.514644	.519218	60010.0
16	1330.0	49.400000	.506276	.507700	79810.0
17	1380.0	48.000000	.502092	.506068	82810.0
18	1880.0	47.000000	.491632	.491238	112800.0
19	2560.0	45.600000	.476987	.474843	153600.0
20	3250.0	44.200000	.462343	.461780	195010.0
21	4100.0	43.000000	.449791	.449467	246010.0

Parameters Utilized in the Simulation

Carbon Mass = 0.7588g

Liquid Volume = 2304 cm^3

ρ_c = 0.75 g/cm^3

D_s = 5.32 E-8 cm^2/sec

k_f = 6.78 E-3 cm/sec

k_b = 1.59 E-6 sec^{-1}

f = 0.708

k = 1.461 $(g/g((g/cm^3)^{**}n))$

n = 0.212

c_o = 9.56 E-5 g/cm^3

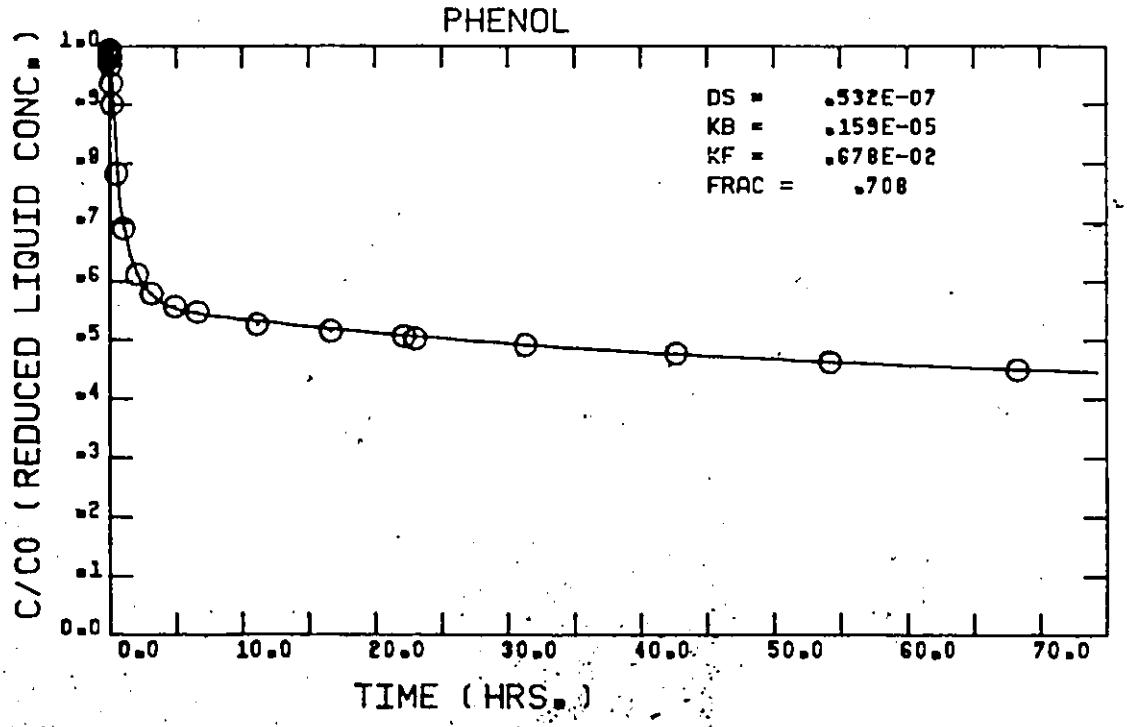

FIGURE F2.1 Simulation of the Phenol Run No. IV from Peel (1980) by the Program SEAR5 which Utilizes the Orthogonal Collocation Method.

APPENDIX F3

PROGRAM FOR THE SINGLE SOLUTE BATCH KINETIC TEST SIMULATIONS (SEAR5)

The program below, called SEAR5, conducts simulations of the single solute batch kinetic tests using the dual rate model described in the text. The program utilizes a one or two section Freundlich isotherm to describe the equilibrium conditions. The solution technique of the equation describing this model were discussed in Section 5.1 and Appendix F1.

The parameter estimation was conducted by an almost identical program called FOX6. The main difference between the two is that the call to subroutine MODEL in SEAR5 is replaced by a call to the regression routine UWHAUS in FOX6. The subroutine UWHAUS, which conducts the non linear least squares regression, itself calls subroutine MODEL. The remaining few changes are in the form of the output. Because of the little difference, program SEAR5 will not be presented in order to avoid repetition.

```
      PROGRAM SEARS (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      COMMON /EQ/ EQ1,EQ2,EQZI,CEP,EQ1P,EQ2P,EQ2PI,FQUE,QUP
      COMMON /AT1/ CHASS,VOL,R,RHOL,FCON
      COMMON /AT2/ DS,KF,KB,F,FF,CEQ,QEQ,CEQCQ
      COMMON /AT3/ BIGF,DIF,BIP,FI,CON,CONTI,CONT2,COR
      COMMON /AT4/ M1,N1,N1M1,N1P1,N2M1,TT,DT,DTT
      COMMON /AT5/ NPROB,NOB,NP
      COMMON /AT6/ N
      COMMON /AT7/ TSEC(60),XMIN(60)
      COMMON /AT8/ XO(110)
      COMMON /AT9/ YY(21)
      COMMON /AT10/ RT(100)
      COMMON /AT11/ CO,CREEP
      DIMENSION TH(4),SIGNS(4),DIFF(4),SCRAT(330)
      DIMENSION COBS(60),CC(110)
      EXTERNAL MODEL,FCN1,FCNJ
      REAL KB,KF
C*****************************************************************C
C                                                                 C
C       PROGRAM SEARS                                             C
C                                                                 C
C       DEVELOPED FOR MODELLING THE  KINETICS OF ACTIVATED CARBON C
C       ADSORPTION IN A BATCH PROCESS.                            C
C                                                                 C
C*****************************************************************C
C-----------------------------------------------------------------------
C  INPUT OF SOME NECESSARY DATA FOR USING SUBROUTINE "UMHAUS", WHICH
C  PERFORMS NONLINEAR LEAST SQUARES REGRESSIONS
      DATA SIGNS(1),SIGNS(2),SIGNS(3),SIGNS(4) /1.,1.,1.,1./
      DATA DIFF(1),DIFF(2),DIFF(3),DIFF(4) / .01,.01,.01,.01 /
      DATA EPS1,EPS2,MIT,FLAM,FNU /1.E-6,1.E-2,20,0.1,10. /
C
C  SUBROUTINE READIN INPUTS THE REMAINING NECESSARY DATA
      CALL READIN
      TH(1)=DS
      IF(NP.GT.2) GO TO 20
      TH(2)=KF
      GO TO 50
   20 TH(2)=KB
      TH(3)=F
      IF(NP.EQ.3) GO TO 50
      TH(4)=KF
   50 CONTINUE
      PRINT*,'TH(1)=',TH(1),' TH(2)=',TH(2),' TH(3)=',TH(3),
     1' TH(4)=',TH(4),' NP=',NP
      DO 100 I=1,NOB
  100 CC(I)=XO(I)
      CALL MODEL(NPROB,TH,CC,NOB,NP)
C
C     SUBROUTINE UMHAUS(NPROB,MODEL,NOB,Y,NP,TH,DIFF,SIGNS,EPS1,EPS2,
C                       MIT,FLAM,FNU,SCRAT)
C     MODEL  - USER SUPPLIED SUBROUTINE TO CALCULATE NU(U), U=1,2,...,NOB
C     NPROB  - PROBLEM NUMBER (USEFUL TO KEEP TRACK OF MODEL WHEN USING SEVERAL
C              DIFFERENT MODELS)
C     NOB    - NUMBER OF OBSERVATIONS
```

```
PROGRAM SEARS      73/738  OPT=2                    FTN 4.8+587        85/07/03
C     Y      - VECTOR OF OBSERVATIONS
C     NP     - NUMBER OF ADJUSTABLE PARAMETERS IN THE MODEL BEING FITTED.
C     TH     - VECTOR OF PARAMETERS. UPON CALLING IT CONTAINS THE INITIAL GUESSES
C              UPON RETURN IT CONTAINS THE LEAST SQUARES ESTIMATES
C     DIFF   - (NP*1) VECTOR OF INCREMENTS TO BE USED IN CALCULATING NUMERICAL
C              DERIVATIVES.  DIFF(I)*TH(I)=INCREMENT USED FOR ITH PARAMETER
C     SIGNS  - (NP*1) VECTOR OF INDICATOR VARIABLES
C              SIGNS(I)=0.   PARAMETER TH(I) CAN CHANGE SIGN
C              SIGNS(I)=1. (OR ANY * NUMBER)   PARAMETER TH(I) IS NOT ALLOWED TO
C                                              CHANGE SIGN
C     EPS1   - ABS VALUE ((SS(J+1)-SS(J))/SS(J)) LESS THAN OR EQUAL TO EPS1
C              THEN STOP ITERATION
C     EPS2   - ABS VALUE ((TH(J+1)-TH(J))/TH(J)) LESS THAN OR EQUAL TO EPS2
C              FOR ALL PARAMETERS TH, THEN STOP
C     MIT    - MAXIMUM NUMBER OF ITERATIONS
C     FLAM   - LAMBDA IN MARQUARDT PROCEDURE
C     FNU    - NU, A FACTOR WHICH DIVIDES LAMBDA UPON EACH SUCCESSFUL ITERATION
C     SCRAT  - DUMMY STORAGE ARRA, MUST BE DIMENSIONED GREATER THAN OR EQUAL TO
C              5*NP + NP**2 + 2*NOB + NP*NOB
C              IT MINIMIZES THE STORAGE SPACE REQUIREMENTS.
C     SUBROUTINE MODEL(NPROB,TH,F,NOB,NP)
C     F      - (NOB*1)  VECTOR OF CALCULATED RESPONSES   NU(U), U=1,2,....,NOB
      STOP
      END
```

```
      SUBROUTINE READIN
      REAL KB,KF
      COMMON /EQ/ EQ1,EQ2,EQ2I,CEP,EQ1P,EQ2P,EQ2PI,FQUE,QUP
      COMMON /AT1/ CMASS,VOL,R,RHOC,FCON
      COMMON /AT2/ DS,KF,KB,F,FF,CE0,QEQ,CEQC0
      COMMON /AT3/ BICF,BIF,BIP,FI,CON,CONT1,CONT2,COR
      COMMON /AT4/ N1,N2,N1M1,N1P1,N2M1,TT,DT,DTT
      COMMON /AT5/ NPROB,NOB,NP
      COMMON /AT6/ N
      COMMON /AT7/ TSEC(60),XMIN(60)
      COMMON /AT8/ XD(110)
      COMMON /AT9/ YT(21)
      COMMON /AT10/ RT(100)
      COMMON /GRATE/ TOL,METH,MITER,MIN
      COMMON /XA/ A(10,10),B(10,10),W(10)
      COMMON /AT11/ C0,CREEP
      DIMENSION COBS(60)
C*****************************************************************************
C
C            -      DEFINITION OF VARIABLES
C
C  C0     - INITIAL CONCENTRATION (GM/CM**3)
C  EQ(1)  - COEFFICIENT OF THE EQUATION FOR THE FREUNDLICH ISOTHERM EQN.
C                 Q=EQ(1)*C**EQ(2) ; ITS UNITS ARE (GM/GM)/(GM/CM**3)**N.
C  EQ(2)  - EXPONENT IN THE EQUATION FOR THE FREUNDLICH ISOTHERM EQN.,
C                 (UNITLESS)
C  F      - FRACTION OF THE TOTAL CAPACITY AVAILABLE DUE TO ADSORPTION
C           IN MACROPORES
C  KB     - BRANCH PORE (MICROPORE) MASS TRANSFER RATE (1/SEC)
C  KF     - EXTERNAL LIQUID FILM TRANSFER COLFFICIENT (CM/SEC)
C  NOB    - NUMBER OF OBSERVATIONS
C  NP     - NUMBER OF ADJUSTABLE PARAMETERS IN THE MODEL BEING FITTED.
C  NPROB  - NUMBER OF THE PROBLEM  (USEFUL TO KEEP TRACK OF THE MODEL
C           BEING USED WHEN ONE IS USING SEVERAL DIFFERENT ONES)
C  QO     - SOLID PHASE REDUCED CONCENTRATION IN EQUILIBRIUM WITH THE
C           THE INFLUENT CONCENTRATION ,CALCULATED BY THE FREUNDLICH
C           ISOTHERM (GRAM POLLUTANT ADSORBED / GRAM OF ACT. CARBON )
C  R      - AVERAGE PARTICLE RADIUS (CM)
C  RHOC   - APPARENT PARTICLE DENSITY (GM/CM**3)
C  TSEC(I)  - TIME AT WHICH OBSERVATION NUMBER I WAS TAKEN (SEC)
C  VOL    - VOLUME OF THE REACTOR (CM**3)
C  CMASS  - MASS OF CARBON IN THE REACTOR (GM)
C  XD(I)  - DIMENSIONLESS CONCENTRATION OF THE OBSERVATION NUMBER I.
C*****************************************************************************
      CALL COEFF(A,B,N,N1M1)
C
      WRITE(6,9)
    9 FORMAT(1H1,10X,"DATA READ IN"//)
      READ(5,*) NPROB,NOB,NP
      READ(5,*) DS,KF,KB,F
      READ(5,*) CMASS,VOL,R,RHOC,C0,CE
      READ(5,*) EQ1,EQ2,CEP,EQ1P,EQ2P
      READ(5,*)N,N1,N2
      READ(5,*) TOL,METH,MITER,MIN
      READ(5,*) TT,DT,DTT
```

```
SUBROUTINE READIN    ? 73/73B  OPT=2                    FTN 4.8+587        85/07/03

      READ(5,*) (YT(I),I=1,N)
C
C  MODEL OF THE FREUNDLICH ISOTHERM
C
      CREEP=CEP
      IF(C0.GT.CEP) GO TO 10
      QEQ=EQ1*CE**EQ2
      Q0=EQ1*C0**EQ2
      GO TO 12
   10 Q0=EQ1P*C0**EQ2P
      QEQ=EQ1P*CE**EQ2P
   12 CONTINUE
      FQUE=1./((EQ2/EQ2P)*(C0**(EQ2-EQ2P)))
      QUP=(EQ1*CE**EQ2)/Q0
      CEQ=CEQC0=CE/C0
      QEQ0=QEQ/Q0
      CEP=CEP/C0
      FCON=VOL/CMASS*C0/Q0
      EQ2I=1./EQ2
      EQ2PI=1./EQ2P
      BICF=C0/(Q0*RHOC)
      N1P1=N1+1
      N1M1=N1-1
      N2M1=N2-1
      FF=1.-F
      PRINT*,"C0      = ",C0," GM/CM**3 = INITIAL CONCENTRATION"
      PRINT*,"Q0      = ",Q0," GM/GM = SOLID PHASE CONCENTRATION IN EQUI
     1LIBRIUM WITH THE INITIAL LIQUID PHASE CONCENTRATION"
      PRINT*,"VOL     = ",VOL," CM**3 = LIQUID VOLUME"
      PRINT*,"CMASS   = ",CMASS," GRAMS = ACTIVATED CARBON MASS"
      PRINT*,"RHOC    = ",RHOC," GM/CM**3 = ACTIVATED CARBON PARTICLE DE
     1NSITY"
      PRINT*,"EQ1     = ",EQ1," GM/GM/((GM/CM**3)**EQ2) = THE COEFFICIEN
```

```
      PRINT*,"EQ1      = ",EQ1," GM/GM/((GM/CM**3)**EQ2) = THE COEFFICIEN
     1T OF THE FREUNDLICH ISOTHERM EQUATION"
      PRINT*,"EQ2      = ",EQ2," DIMENSIONLESS =  THE EXPONENT OF THE FRE
     1UNDLICH ISOTHERM"
      PRINT*,"CEP      = ",CEP
      PRINT*,"CREEP    = ",CREEP
      PRINT*,"EQ1P     = ",EQ1P
      PRINT*,"EQ2P     = ",EQ2P
      PRINT*,"EQ2PI    = ",EQ2PI
      PRINT*,"QUP      = ",QUP
      PRINT*,"PQUE     = ",PQUE
      PRINT*,"R        = ",R," CM = RADIUS OF ACTIVATED CARBON PARTICLES"
      PRINT*,"DS       = ",DS," CM**2/SEC = THE SURFACE DIFFUSION COEFFIC
     1IENT"
      PRINT*,"KF       = ",KF," CM/SEC = EXTERNAL LIQUID FILM TRANSFER CO
     1EFFICIENT"
      PRINT*,"KB       = ",KB," (1./SEC) = MICROPORE RATE COEFFICIENT"
      PRINT*,"F        = ",F," MACROPOROUS FRACTION"
      PRINT*,"TT       = ",TT," HOURS = TOTAL TIME"
      PRINT*,"DTI      = ",DTI," MIN. = DIFFERENTIAL TIME STEP SIZE"
      PRINT*,"DTT      = ",DTT," (MIN.) = INITIAL DIFF. TIME STEP"
      PRINT*,"FCON     = ",FCON
      PRINT*,"BIGF     = ",BIGF
      PRINT*,"NOB      = ",NOB," = NUMBER OF OBSERVATIONS"
      PRINT*,"N        = ",N," = NUMBER OF O.D.E.'S BEING SOLVED"
      PRINT*,"N1       = ",N1," = TOTAL NUMBER OF COLLOCATION POINTS"
      PRINT*,"N2       = ",N2," = TWICE N1"
      PRINT*,"NPROB    = ",NPROB," = PROBLEM NUMBER"
      PRINT*,"NP       = ",NP," =NUMBER OF PARAMETERS REGRESSED"
      PRINT*,"CE       = ",CE," GM/CM**3 = EQUILIBRIUM LIQUID PHASE CONCE
     1NTRATION"
      PRINT*,"QEQ      = ",QEQ,"   GM/GM= EQUILIBRIUM REDUCED SOLID PHASE
     1 CONCENTRATION"
      PRINT*,"QEQO     = ",QEQO
      PRINT*,"CEQCO    = ",CEQCO," = REDUCED EQUILIBRIUM LIQUID PHASE CON
     1CENTRATION"
      PRINT*,"EQ2I     = ",EQ2I," = THE INVERSE OF EQ2"
      PRINT*,"TOL      = ",TOL
      PRINT*,"METH     = ",METH
      PRINT*,"MITER    = ",MITER
      PRINT*,"MIN      = ",MIN
      WRITE(6,15)
   15 FORMAT("1",/,14X,"CONCENTRATION",5X,"REDUCED",12X,"TIME"/
     1/" ",1X,"I",4X,"MINUTES",2X,"(MICROG/L)",7X,"CONCEN.",12X,"(SEC.)"
     2/)
      DO 20 J=1,NOB
      READ(5,*) XMIN(J),COBS(J),TSEC(J)
      XO(J)=COBS(J)/(CO*1.E+6)
      RT(J)=TSEC(J)
      WRITE(6,30) J,XMIN(J),COBS(J),XO(J),TSEC(J)
   20 CONTINUE
   30 FORMAT(" ",I3,2X,F8.1,2X,F18.6,2X,F12.6,2X,F16.1)
      WRITE(6,1000)
 1000   FORMAT(1H1//" PROGRAM ACKINE OUTPUT"///)
      RETURN
      END
```

```
      SUBROUTINE MODEL(NPROB,TH,CM,NOB,NP)
      DIMENSION WK(300),IWK(21)
      DIMENSION Y(21),YPRIME(21)
      DIMENSION TH(4),TRT(100),CM(110)
      DIMENSION XWRK(4,21),YEND(21)
      DIMENSION Z(45,11)
      REAL KF,KB
      EXTERNAL FCN1,FCNJ
      COMMON /AT1/ CMASS,VOL,R,RHOC,FCON
      COMMON /AT2/ DS,KF,KB,F,FF,C1,Q,QEQ,CEQCO
      COMMON /EQ/ EQ1,EQ2,EQ2I,EQ2P,CEQI,EQ1P,EQ2PI,FQUE,QUP
      COMMON /AT3/ BIF,BIF,BIP,F1,CON,CONT1,CONT2,COR
      COMMON /AT4/ M1,M2,M1M1,M1P1,M2M1,TT,DT,DTT
      COMMON /AT6/ N
      COMMON /AT7/ TSEC(68),XMIN(68)
      COMMON /AT8/ XOT(10)
      COMMON /AT9/ YT(21)
      COMMON /AT10/ RT(100)
      COMMON /AT11/ CO,CREEP
      COMMON /XA/ A(10,10),B(10,10),W(10)
      COMMON /GRATE/ TOL,METH,MITER,MIN
      COMMON /GEAR/ RUMMY(48),ROUMSY(6),IRUMMY(38)
      M=MIN
      DS=TH(1)
      IF(NP.GT.2) GO TO 5011
      KF=TH(2)
      GO TO 5012
 5011 KB=TH(2)
      F=TH(3)
      IF(NP.EQ.3) GO TO 5012
      KF=TH(4)
 5012 CONTINUE
      PRINT*,"IN MODEL, DS=",DS," KB=",KB," F=",F," KF=",KF
      TF=DS/R**2
      DO 17 JT=1,NOB
   17 TRT(JT)=RT(JT)*TF
      DO 18 JIN=1,N
   18 Y(JIN)=YT(JIN)
      PRINT*," INITIAL Y = ",(Y(KUTE),KUTE=1,N)
      BIP=KB*R**2/DS
      BIF=3*KF*R/DS
      FF=1.-F
      F1=CMASS/(VOL*RHOC)
      IF(F.EQ.1.000) FF=1.000
      CON=BIF*BIF/(3.*F)
      COR=F1*BIF
      CONT2=BIP/F
      CONT1=BIP/FF
      DXS=DTT*60.0*TF
      DXOLD=DXS
      DXROLD=DXCLD
      X=0.0
      INDEX=1
      NN=N
      METH=2
      MITER=3
```

```
SUBROUTINE MODEL      73/730  OPT=2                    FTN 4.8+587        85/07/0
C*****************************************************************C
C                                                                 C
      DO 67 K=1,NOB
      XMINN=XMIN(K)
      XEND=TRT(K)
      XOLD=X
      DX=XEND-X
      PRINT*,"  XEND=",XEND," XMIN=",XMIN(K)," M=",M," X=",X,
     1" INDEX=",INDEX," TOL=",TOL," METH=",METH," MITER=",MITER
      IFFY=0
      ITRACK=0
      T=X/TF/60.0
      IF(K.EQ.1) GO TO 448
      IF(XMIN(K).EQ.XMIN(K-1)) GO TO 446
  448 CONTINUE
      CALL DGEAR(N,FCN1,FCNJ,X,N,Y,XEND,TOL,METH,MITER,INDEX,IWK,
     1WK,IER)
  446 CONTINUE
      T=X/TF/60.0
      PRINT*,"  T=",T," X=",X," DX=",DX," Y(NZ)=",Y(NZ)," Y(N)=",Y(N)
      CS=Y(NZ)**EQ2P
      IF(Y(NZ).LT.QUP) CS=FQUE*Y(NZ)**EQ2I
      IF(CS.LT.CREEP) CS=Y(NZ)**EQ2I
      XMINN=XMIN(K)
      CM(K)=Y(N)
      GNCHEK=0.0
      GBCHEK=0.0
      DO 866 IKM=1,M1
      IOP=IKM+M1
      GNCHEK=GNCHEK+W(IKM)*Y(IOP)
      GBCHEK=GBCHEK+W(IKM)*Y(IKM)
  866 CONTINUE
      GNCHEK=GNCHEK*3.
```

```
      QBCHEK=QBCHEK*3.
      QCHECK=(QMCHEK*F+QBCHEK*FF)
      Z(K,1)=XO(K)
      Z(K,2)=Y(N)
      Z(K,3)=CS
      Z(K,4)=T
      Z(K,5)=Y(N2)
      Z(K,6)=QCHECK
      Z(K,7)=FF*Y(N1)+F*Y(N2)
      Z(K,8)=QMCHEK
      Z(K,9)=QBCHEK
      Z(K,10)=FCON*(1.0-Y(N))
      Z(K,11)=Y(N1-XO(K)
      PRINT*,"  K=",K,"  T=",T,"  XO(K)=",XO(K),"  Y(N)=",Y(N)
      PRINT*,"QMCHEK=",QMCHEK,"  QBCHEK=",QBCHEK,"  QCHECK=",QCHECK,"  CS="
     1,CS
      PRINT*,"XMIN(K)=",XMIN(K),"  Y(JJJ)=",(Y(JJJ),JJJ=1,N)
      PRINT*,"  H=",H,"  XEND=",XEND,"  X=",X,"  INDEX=",INDEX,"  IFFY="
     1,IFFY,"  NFE=",IRUMMY(8),"  NJ=",IRUMMY(9),"  NSTEP=",IRUMMY(7)
      IF(IER.GT.128) GO TO 20
   67 CONTINUE
      SS=0.0000
      DO 670 K=1,NOB
  670 SS=SS+(XO(K)-CH(K))**2
      PRINT*,"-----------KB=",KB,"  F=",F,"  DS=",DS,"  SS=",SS
      WRITE(6,921)
  921 FORMAT(1H1,15X,"  FINAL RESULTS"//)
      WRITE(6,930)
      WRITE(6,931)
      DO 922  K=1,NOB
      WRITE(6,940)(Z(K,I),I=1,11)
  922 CONTINUE
  930 FORMAT(" ","  XO",4X,"PREDICTED",4X,"  CS",4X,"TIME",6X,"QS",5X,"TOT
     1AL Q",5X,"QS",8X,"QM",6X,"QB",4X,"MASS BAL.",4X,"ERROR")
  931 FORMAT(" ",26X,"(MIN.)",3X,"(MICRO-)",4X,"TOTAL")
  940 FORMAT(" ",F6.3,1X,F9.6,1X,F8.6,1X,F7.1,7(1X,F8.5))
      RETURN
   20   PRINT*,"  TROUBLE ---   IER = ",IER
      STOP
      END
```

```
      SUBROUTINE FCN1(N,X,Y,YPRIME)
      REAL  Y(N),YPRIME(N),X
      REAL  MURRY,KF,KB
      COMMON /AT1/ CMASS,VOL,R,RHOC,FCON
      COMMON /EQ/ EQ1,EQ2,EQ2I,CEP,EQ1P,EQ2P,EQ2PI,FQUE,QUP
      COMMON /AT2/  QS,KF,KB,F,FF,CLQ,QEQ,QEQCO
      COMMON /AT3/ BIGF,BIF,BIP,P1,CON,CONT1,CONT2,COR
      COMMON /AT4/ N1,N2,N1P1,N1P1,N2M1,TT,DT,DTT
      COMMON /AT5/ NPROB,NOB,MP
      COMMON /AT11/ CQ,CREEP
      COMMON /A1/ A(10,10),B(10,10),W(10)
      CS=Y(N2)**EQ2P1
      IF(Y(N2).LT.QUP) CS=FQUE*Y(N2)**EQ2I
      IF(CQ.LT.CREEP) CS=Y(N2)**EQ2I
      DO 50 JT=1,N1
      NEXT=N1+JT
   50 YPRIME(JT)=CONT1*(Y(NEXT)-Y(JT))
      DO 51 JU=N1P1,N2M1
      NOWP=JU-N1
      YPRIME(JU)=0.0
      DO 52 JV=N1P1,N2
      JVV=JV-N1
      YPRIME(JU)=YPRIME(JU)+B(NOWP,JVV)*Y(JV)
   52 CONTINUE
      YPRIME(JU)=YPRIME(JU)-CONT2*(Y(JU)-Y(NOWP))
   51 CONTINUE
      YPRIME(N2)=CON*(Y(N)-CS)
      DO 79 KAT=1,N1
      KOT=KAT+N1
   79 YPRIME(N2)=YPRIME(N2)-W(KAT)*CONT2*(Y(KOT)-Y(KAT))
      MURRY=0.0
      DO 80 KORT=1,N1N1
      KART=KORT+N1
      MURRY=MURRY+YPRIME(KART)*W(KORT)
   80 CONTINUE
      YPRIME(N2)=(1./W(N1))*(YPRIME(N2)-MURRY)
      YPRIME(N)=COR*(Y(N)-CS)
      RETURN
      END
```

```
      SUBROUTINE COEFF(A,B,VECT,NMIN)
      DIMENSION DIF1(10),DIF2(10),DIF3(10),ROOT(10),VECT(10),X(10)
      REAL L1(10,10),L2(10,10),A(10,10),B(10,10)
      INTEGER SMALLA
      READ*,SMALLA
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
C         FOR SLAB GEOMETRY         SMALLA=1        ALPHA=1        BETA=-0.5
C  FOR CYLINDRICAL GEOMETRY         SMALLA=2        ALPHA=1        BETA=0.0
C    FOR SPHERICAL GEOMETRY         SMALLA=3        ALPHA=1        BETA=0.5
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
      GO TO(401,402,403),SMALLA
  401 BE=-0.5
      AL=1.0000
      GO TO 404
  402 BE=0.0
      AL=1.0000
      GO TO 404
  403 BE=0.5
      AL=1.0000
  404 CONTINUE
      READ*,NMIN,NMAX
      PRINT *,"NMIN=",NMIN
      PRINT *,"NMAX=",NMAX
      DO 9 N=NMIN,NMAX
      PRINT 100,AL,BE,N
  100 FORMAT("1",10X,"GAUSS-JACOBI QUADRATURE , ALPHA=",F6.2,3X
     1,"BETA=",F6.2,3X,"N=",I3///)

      NO=0
      N1=1
      NT=N+NO+N1
      PRINT 207
  207 FORMAT(" "//10X,"ROOTS OF NODE POLYNOMIAL WHEN NO=0 , N1=1"/)
      CALL JACOBI(NT,N,NO,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
      PRINT *,(ROOT(J),J=1,NT)
      PRINT 500
  500 FORMAT(" "//10X,"THE VALUES OF THE X'S"/)
      DO 150 I=1,NT
      X(I)=SQRT(ROOT(I))
  150 CONTINUE
      PRINT*,(X(J),J=1,NT)
      PRINT 201
  201 FORMAT(" "//10X,"FIRST THREE DERIVATIVES OF NODE POLYNOMIAL"/)
      PRINT *,(DIF1(J),J=1,NT)
      PRINT *,(DIF2(J),J=1,NT)
      PRINT *,(DIF3(J),J=1,NT)

      PRINT 202
  202 FORMAT(" "//10X,"FIRST DERIVATIVES OF LI(X) - MATRIX A"/)
      ID=1
      DO 5 J=1,NT
      CALL DFOPR(NT,N,NO,N1,J,ID,DIF1,DIF2,DIF3,ROOT,VECT)
      PRINT *,(VECT(K),K=1,NT)
      DO 250 I=1,NT
  250 L1(J,I)=VECT(I)
    5 CONTINUE
      PRINT 203
  203 FORMAT(" "//10X,"SECOND DERIVATIVES OF LI(X) - MATRIX B"/)
      ID=2
      DO 6 J=1,NT
      CALL DFOPR(NT,N,NO,N1,J,ID,DIF1,DIF2,DIF3,ROOT,VECT)
      PRINT *,(VECT(K),K=1,NT)
      DO 255 I=1,NT
  255 L2(J,I)=VECT(I)
    6 CONTINUE

      ID=1
      CALL RADAU(NT,N,NO,N1,ID,AL,BE,ROOT,DIF1,VECT)
      IF(SMALLA.EQ.1) GO TO 710
      DO 705 JIK=1,NT
      IF(SMALLA.EQ.2) VECT(JIK)=VECT(JIK)/2.
      IF(SMALLA.EQ.3) VECT(JIK)=VECT(JIK)/3.
  705 CONTINUE
  710 CONTINUE
      PRINT 206
  206 FORMAT(" "//10X,"RADAU WEIGHTS"/)
      PRINT *,(VECT(J),J=1,NT)

      PRINT 290
  290 FORMAT(" "//10X," THE MATRIX 'A' , AS IN VILLADSEN AND STEWART
     1(1967)")
      DO 310 KI=1,NT
      DO 300 KJ=1,NT
      A(KI,KJ)=2.*X(KI)*L1(KI,KJ)
      B(KI,KJ)=4.*X(KI)**2*L2(KI,KJ)+2.*L1(KI,KJ)
      IF(SMALLA.EQ.2) B(KI,KJ)=B(KI,KJ)+A(KI,KJ)/X(KI)
      IF(SMALLA.EQ.3) B(KI,KJ)=B(KI,KJ)+2./X(KI)*A(KI,KJ)
  300 CONTINUE
      PRINT *,(A(KI,KJT),KJT=1,NT)
  310 CONTINUE
      PRINT 220
  220 FORMAT(" "//10X," THE MATRIX 'B' , AS IN VILLADSEN AND STEWART
     1(1967)")
      DO 350 KIP=1,NT
      PRINT *,(B(KIP,KJT),KJT=1,NT)
  350 CONTINUE
    9 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE JACOBI(ND,N,NO,N1,AL,BE,DIF1,DIF2,DIF3,ROOT)
      DIMENSION DIF1(ND),DIF2(ND),DIF3(ND),ROOT(ND)
C
C     EVALUATION OF ROOTS AND DERIVATIVES OF JACOBI POLYNOMIALS
C     P(N) (AL,BE)
C
C     FIRST EVALUATION OF COEFFICIENTS IN RECURSION FORMULAE
C     RECURSION COEFFICIENTS ARE STORED IN DIF1 AND DIF2
C
      AB=AL+BE
      AD=BE-AL
      AP=BE*AL
      DIF1(1)=(AD/(AB+2.)+1.)/2.
      DIF2(1)=0.
      IF(N.LT.2) GO TO 15
      DO 10  I=2,N
      Z1=I-1
      Z=AB+2.*Z1
      DIF1(I)=(AB*AD/Z/(Z+2.)+1.)/2.
      IF(I.NE.2)  GO TO 11
      DIF2(I)=(AB+AP+Z1)/Z/Z/(Z+1.)
      GO TO 10
   11 CONTINUE
      Z=Z*Z
      Y=Z1*(AB+Z1)
      Y=Y*(AP+Y)
      DIF2(I)=Y/Z/(Z-1.)
   10 CONTINUE
C
C     ROOT DETERMINATION BY NEWTON METHOD WITH SUPPRESSION
C     OF PREVIOUSLY DETERMINED ROOTS
C
   15 CONTINUE
      X=0.
      DO 20  I=1,N
   25 CONTINUE
      XD=0.
      XN=1.
      XD1=0.
      XN1=0.
      DO 30  J=1,N
      XP=(DIF1(J)-X)*XN-DIF2(J)*XD
      XP1=(DIF1(J)-X)*XN1-DIF2(J)*XD1-XN
      XD=XN
      XD1=XN1
      XN=XP
      XN1=XP1
   30 CONTINUE
      ZC=1.
      Z=XN/XN1
      IF(I.EQ.1) GO TO 21
      DO 22  J=2,I
      ZC=ZC-Z/(X-ROOT(J-1))
   22 CONTINUE
   21 CONTINUE
      Z=Z/ZC
      X=X-Z
      IF(ABS(Z).GT.1.E-9) GO TO 25
      ROOT(I)=X
      X=X+.0001
   20 CONTINUE
C
C     ADD EVENTUAL INTERPOLATION POINTS AT X=0 OR X=1
C
      NT=N+ND+N1
      IF(ND.EQ.0) GO TO 35
      DO 31  J=1,N
      JJ=N+1-J
      ROOT(JJ+1)=ROOT(J)
   31 CONTINUE
      ROOT(1)=0.
   35 CONTINUE
      IF(N1.EQ.1) ROOT(NT)=1.
C
C     NOW EVALUATE DERIVATIVES OF POLYNOMIAL
C
      DO 40  I=1,NT
      X=ROOT(I)
      DIF1(I)=1.
      DIF2(I)=0.
      DIF3(I)=0.
      DO 40  J=1,NT
      IF(J.EQ.I) GO TO 40
      Y=X-ROOT(J)
      DIF3(I)=Y*DIF3(I)+3.*DIF2(I)
      DIF2(I)=Y*DIF2(I)+2.*DIF1(I)
      DIF1(I)=Y*DIF1(I)
   40 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE DFOPR(ND,N,M0,M1,I,ID,DIF1,DIF2,DIF3,ROOT,VECT)
      DIMENSION DIF1(ND),DIF2(ND),DIF3(ND),ROOT(ND),VECT(ND)
C
C     SUBROUTINE EVALUATES DISCRETIZATION MATRICES AND
C     GAUSSIAN QUADRATURE WEIGHTS , NORMALIZED TO SUM 1
C     ID=1 ;  DISCRETIZATION MATRIX FOR Y(1)  (X)
C     ID=2 ;  DISCRETIZATION MATRIX FOR Y(2)  (X)
C     ID=3 ;  GAUSSIAN QUADRATURE WEIGHTS
C
      MT=N+M0+M1
      IF(ID.EQ.3) GO TO 10
      DO 20 J=1,MT
      IF(J.NE.I) GO TO 21
      IF(ID.NE.1) GO TO 5
      VECT(I)=DIF2(I)/DIF1(I)/2.
      GO TO 20
    5 CONTINUE
      VECT(I)=DIF3(I)/DIF1(I)/3.
      GO TO 20
   21 CONTINUE
      Y=ROOT(I)-ROOT(J)
      VECT(J)=DIF1(I)/DIF1(J)/Y
      IF(ID.EQ.2) VECT(J)=VECT(J)*(DIF2(I)/DIF1(I)-2./Y)
   20 CONTINUE
      GO TO 50
   10 CONTINUE
      Y=0.
      DO 25 J=1,MT
      X=ROOT(J)
      AX=X*(1.-X)
      IF(M0.EQ.0) AX=AX/X/X
      IF(M1.EQ.0) AX=AX/(1.-X)/(1.-X)
      VECT(J)=AX/DIF1(J)**2
      Y=Y+VECT(J)
   25 CONTINUE
      DO 60 J=1,MT
      VECT(J)=VECT(J)/Y
   60 CONTINUE
   50 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE RADAU(ND,N,M0,M1,ID,AL,BE,ROOT,DIF1,VECT)
      DIMENSION ROOT(ND),DIF1(ND),VECT(ND)
C
C     RADAU AND LOBATTO QUADRATURE WEIGHTS
C       ID = 1 ; RADAU QUADRATURE WITH X=1.
C       ID = 2 ; RADAU QUADRATURE WITH X=0.
C       ID = 3 ; LOBATTO QUADRATURE WITH BOTH ENDPOINTS
C
      S=0.
      MT=N+M0+M1
      DO 40 I=1,MT
      X=ROOT(I)
      IF(ID-2) 10,20,30
   10 CONTINUE
      AX=X
      IF(M0.EQ.0) AX=1./AX
      GO TO 40
   20 CONTINUE
      AX=1.-X
      IF(M1.EQ.0) AX=1./AX
      GO TO 40
   30 CONTINUE
      AX=1.
   40 VECT(I)=AX/DIF1(I)**2
      IF(ID.NE.2) VECT(MT)=VECT(MT)/AL
      IF(ID.GT.1) VECT(1)=VECT(1)/BE
      DO 50 I=1,MT
      S=S+VECT(I)
   50 CONTINUE
      DO 60 I=1,MT
      VECT(I)=VECT(I)/S
   60 CONTINUE
      RETURN
      END
```

APPENDIX F4

PROGRAM FOR THE BISOLUTE BATCH KINETIC TEST SIMULATION (ZORRO3)

The program ZORRO3, listed below, simulates the adsorption of two solutes in batch kinetic tests, in a procedure analogous to that of the single component. The program was based on the HSSD model for bisolute mixtures with diffusional interactions within the particle, described in Section 5.3. ZORRO3 also includes terms which account for solutes requiring the dual rate model. This program utilizes MSCAM to describe the equilibrium conditions assumed to occur at the surface of the particles.

ZORRO3 has an analogous program called FOX23 which conducts a multiresponse regression in order to obtain the values of the cross diffusion coefficients. FOX23 uses the multiresponse regression routine MVEST developed by Jutan (1976), but otherwise is almost identical to ZORRO3, and so it will not be listed in this thesis.

```
PROGRAM ZORRO3     73/738  OPT=2                                  FTN 4.8+587          85/07/2
      PROGRAM ZORRO3 (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      COMMON /ZT1/ DS1,DS2,KF1,KF2,KB1,KB2,F1,F2,BIGF1,BIGF2
      COMMON /ZT2/ CON1,CON2,COR1,COR2,COB1,COB2,COM1,COM2,COS
      COMMON /ZT4/ N1,N2,NS1,NS2,NL1,NMIN
      COMMON /ZT5/ TT,DT,OTT
      COMMON /ZT7/ NJ1,NJ2,NJ21,NJ22,NJ31,NJ32
      COMMON /ZT8/CO1,CO2,OO1,OO2,WW1,WW2,FQUE,HKEY,XKEY
      COMMON /ZT9/ AQ,AQP,BQ
      COMMON /ZT10/ KOOT1,KOOT1P,KOOT2,EEQ1I,EEQ1PI,EEQ2I,QUP1
      COMMON /AT1/ CMASS,VOL,R,RHOC,FCON
      COMMON /AT5/ NPROB,NOB,NP
      COMMON /AT6/ N
      COMMON /AT7/ TSEC(110),XMIN(110)
      COMMON /AT8/ XD1(110),XD2(110)
      COMMON /AT9/ YY(20)
      COMMON /AT10/ RT(100)
      COMMON /POW/ NSIG,NNN,ITMAX,PAR(30)
      COMMON /TOK/ CS1OLD,CS2OLD,CS1,CS2,XTK1,XTK2
      COMMON /CROSS/ DS12,DS21,KB12,KB21
      COMMON /NC/ NCOL,NCOL1,NCOL2,NCOL3,NCOL4,NCOL5,NCOL6,NCOL1P
     1,NCOL2P,NCOL2M,NCOL5M,NCOL1M
      COMMON /ZAP/ COM12,COM21,COB12,COB21
      DIMENSION TH(8)
      DIMENSION COBS1(60),COBS2(60),CC1(110),CC2(110)
      EXTERNAL MODEL,FCN1,FCNISO
      REAL KB1,KB2,KF1,KF2,WW1,WW2,KB12,KB21
      REAL KOOT1,KOOT1P,KOOT2
C*****************************************************************
C                                                                 C
C       PROGRAM ZORRO3                                            C
C                                                                 C
C       DEVELOPED FOR MODELLING THE  KINETICS OF ACTIVATED CARBON C
C       ADSORPTION OF TWO COMPETING COMPOUNDS IN A BATCH          C
C       EXPERIMENT                                                C
C                                                                 C
C*****************************************************************
C
C  SUBROUTINE READIN INPUTS THE REMAINING NECESSARY DATA
      CALL READIN
      TH(1)=DS1
      TH(2)=KB1
      TH(3)=F1
      TH(4)=KF1
      TH(5)=DS2
      TH(6)=KB2
      TH(7)=F2
      TH(8)=KF2
      TMAX=TT*3600.
      DLT=TMAX/100.
      NOG=100
      DO 40 I=1,NOG
   40 RT(I)=FLOAT(I)*DLT
      CALL MODEL(NOB,NPROB,TH,CC1,CC2,NOG,NP)
      DO 100 I=1,NOB
      TIME=TSEC(I)
      CONC1=XD1(I)
      CALL PLOTPT(TIME,CONC1,4)
  100 CONTINUE
      DO 110 I=1,100
      TIME=RT(I)
      CONC1=CC1(I)
      WRITE(6,150) XMIN(I),CC1(I),CC2(I),XMIN(I)
      CALL PLOTPT(TIME,CONC1,9)
  110 CONTINUE
      CALL OUTPLT
      DO 120 I=1,NOB
      TIME=TSEC(I)
      CONC2=XD2(I)
      CALL PLOTPT(TIME,CONC2,4)
  120 CONTINUE
      DO 130 I=1,100
      TIME=RT(I)
      CONC2=CC2(I)
      CALL PLOTPT(TIME,CONC2,9)
  130 CONTINUE
      CALL OUTPLT
      CALL DATAPLT(NPROB,TH,XD1,NOB,NP,CC1,NOG)
      TH(1)=TH(5)
      TH(2)=TH(6)
      TH(3)=TH(7)
      TH(4)=TH(8)
      CALL DATAPLT(NPROB,TH,XD2,NOB,NP,CC2,NOG)
      CALL PLOT(0.0,0.0,999)
C
C
  150 FORMAT(" ",2X,F7.0,2X,F9.6,2X,F9.6,2X,F7.0)
      STOP
      END
```

```
      SUBROUTINE READIN
      REAL KB1,KB2,KF1,KF2,MW1,MW2,G(2),KB12,KB21
      REAL KOOT1,KOOT1P,KOOT2
      COMMON /IT1/ DS1,DS2,KF1,KF2,KB1,KB2,F1,F2,BIGF1,BIGF2
      COMMON /IT2/ CON1,CON2,COR1,COR2,C01,C02,CON1,CON2,CDS
      COMMON /IT4/ M1,M2,MS1,MS2,MI1,MMIN
      COMMON /IT5/ TT,DT,DTT
      COMMON /IT7/ MI1,MI2,MI21,MI22,MJ1,MJ2
      COMMON /IT8/C01,C02,Q01,Q02,MW1,MW2,FQUE,MKEY,XKEY
      COMMON /IT9/ AQ,AQP,BQ
      COMMON /IT10/ KOOT1,KOOT1P,KOOT2,EEQ1I,EEQ1PI,EEQ2I,QUP1
      COMMON /AT1/ CPASS,VOL,R,RHOC,FCON
      COMMON /AT5/ NPROB,NOB,NP
      COMMON /AT6/ N
      COMMON /AT7/ TSEC(110),XMIN(110)
      COMMON /AT8/ XD1(110),XD2(110)
      COMMON /AT9/ YI(26)
      COMMON /AT10/ AI(108)
      COMMON /POW/ NSIG,MNN,ITMAX,PAR(30)
      COMMON /TOW/ CS1OLD,CS2OLD,CS1,CS2,XTK1,XTK2
      COMMON /BT7/ TOL, METH, MITER, MSTART
      COMMON /XA/ A(10,10), B(10,10), W(10)
      COMMON /CROSS/ DS12,DS21,KB12,KB21
      COMMON /NC/ NCCL,NCOL1,NCOL2,NCOL3,NCOL4,NCOL5,NCOL6,NCOL1P
     1,NCOL3P,NCCL2M,NCOL5M,NCOL1M
      DIMENSION COBS1(60), COBS2(60)
C*****************************************************************
C
C                  DEFINITION OF VARIABLES
C
C  CO      - INITIAL CONCENTRATION (GM/CM**3)
C  EQ(1)   - COEFFICIENT OF THE EQUATION FOR THE FREUNDLICH ISOTHERM EQN.
C                 Q=EQ(1)*C**EQ(2) , ITS UNITS ARE (GM/GM)/(GM/CM**3)**N
C  EQ(2)   - EXPONENT IN THE EQUATION FOR THE FREUNDLICH ISOTHERM EQN.
C                 (UNITLESS)
C  F       - FRACTION OF THE TOTAL CAPACITY AVAILABLE DUE TO ADSORPTION
C            IN MACROPORES
C  KB      - BRANCH PORE (MICROPORE) MASS TRANSFER RATE (1/SEC)
C  KF      - EXTERNAL LIQUID FILM TRANSFER COEFFICIENT (CM/SEC)
C  NOB     - NUMBER OF OBSERVATIONS
C  NP      - NUMBER OF ADJUSTABLE PARAMETERS IN THE MODEL BEING FITTED.
C  NPROB   - NUMBER OF THE PROBLEM  (USEFUL TO KEEP TRACK OF THE MODEL
C              BEING USED WHEN ONE IS USING SEVERAL DIFFERENT ONES)
C  QO      - SOLID PHASE REDUCED CONCENTRATION IN EQUILIBRIUM WITH THE
C            THE INFLUENT CONCEMTRATION ,CALCULATED BY THE FREUNDLICH
C            ISOTHERM (GRAM POLLUTANT ADSORBED / GRAM OF ACT. CARBON )
C  R       - AVERAGE PARTICLE RADIUS (CM)
C  RHOC    - APPARENT PARTICLE DENSITY (GM/CM**3)
C  TSEC(I) - TIME AT WHICH OBSERVATION NUMBER I WAS TAKEN (SEC)
C  VOL     - VOLUME OF THE REACTOR (CM**3)
C  CMASS   - MASS OF CARBON IN THE REACTOR (GM)
C  XD(I)   - DIMENSIONLESS CONCENTRATION OF THE OBSERVATION NUMBER I
C*****************************************************************
      CALL COEFF(A,B,W,NMIN)
C
      READ(5,*) MKEY
      READ(5,*) NSIG,MNN,ITMAX
      READ(5,*) NPROB,NOB,NP
      READ(5,*) DS1,KB1,F1,KF1
      READ(5,*) DS2,KB2,F2,KF2
      READ(5,*) MW1,MW2
      READ(5,*) CMASS,VOL,R,RHOC
      READ(5,*) C01,C02,CNON1
      READ(5,*) EQ1,EEQ1,EQ1P,EEQ1P,EQ2,EEQ2,CEP
      READ(5,*) FAC1,FAC2
      READ(5,*) M1,M2,N
      READ(5,*) TT,DT,DTT
      READ(5,*) (YI(I),I=1,N)
      READ(5,*)CS1OLD,CS2OLD
      READ(5,*) TOL, METH, MITER, MSTART
      READ(5,*) DS12,DS21,KB12,KB21
C
C MODEL OF THE FREUNDLICH ISOTHERM
C
      PRINT*,"MKEY      = ",MKEY
      PRINT*,"CEP     = ",CEP," (GM/CM**3)"
      PRINT*,"C01     = ",C01," (GM/CM**3)"
      PRINT*,"CNON1   = ",CNON1," (GM/CM**3) = NON-ADSORBABLE ORGANICS"
      CEP=CEP-CNON1
      Q02=EQ2*C02**EEQ2
      C01=C01-CNON1
      IF(C01.GT.CEP) GO TO 10
      Q01=EQ1*C01**EEQ1
      GO TO 12
   10 Q01=EQ1P*C01**EEQ1P
   12 CONTINUE
      QUP1=(EQ1*CEP**EEQ1)/Q01
      FQUE=1./((EQ1/EQ1P)*(C01**(EEQ1-EEQ1P)))
      CEP=CEP/C01
      EEQ1I=1./EEQ1
      EEQ1PI=1./EEQ1P
      EEQ2I=1./EEQ2
      BIGF1=C01/(Q01*RHOC)
      BIGF2=C02/(Q02*RHOC)
      MS1=M1-1
      MS2=M2-1
```

```
      KDOT1=EQ1*(MW1**EEQ1)/MW1
      KDOT1P=EQ1P*(MW1**EEQ1P)/MW1
      KDOT2=EQ2*(MW2**EEQ2)/MW2
      PAR(14)=CEP*CB1/MW1
      PAR(3)=EEQ1
      PAR(4)=EEQ2
      PAR(7)=EEQ1P
      PAR(1)=(1.-FAC1)*KDOT1
      PAR(2)=(1.-FAC2)*KDOT2
      PAR(10)=(1.-FAC1)*KDOT1P
      PAR(18)=FAC1*KDOT1
      PAR(19)=FAC2*KDOT2
      PAR(12)=FAC1*KDOT1P
      PAR(20)=(EEQ1+EEQ2)/2.
      PAR(21)=(EEQ1P+EEQ2)/2.
      PAR(22) = 1 / PAR(20)
```

SUBROUTINE READIN 73/738 OPT=2 FTN 4.8+587 85/07/25

```
      PAR(23) = 1 / PAR(21)
      PAR(24) = SQRT(PAR(18) * PAR(19))
      PAR(25) = SQRT(PAR(12) * PAR(19))
      PAR(11) = PAR(20) - 1
      PAR(13) = PAR(21) - 1
      PAR(15) = PAR(18) / PAR(24)
      PAR(16) = PAR(19) / PAR(24)
      PAR(17) = PAR(12) / PAR(25)
      PAR(26) = PAR(19) / PAR(25)
      PAR(27) = PAR(24) ** (PAR(20) - PAR(22))
      PAR(28) = PAR(25) ** (PAR(21) - PAR(23))

      PRINT*,"CB1       = ",CB1," GM/CM**3 = INITIAL CONCENTRATION"
      PRINT*,"CB2       = ",CB2," GM/CM**3 = INITIAL CONCENTRATION"
      PRINT*,"Q01       = ",Q01," GM/GM = SOLID PHASE CONCENTRATION IN
     1EQUILIBRIUM WITH THE INITIAL LIQUID PHASE CONCENTRATION"
      PRINT*,"Q02       = ",Q02," GM/GM = SOLID PHASE CONCENTRATION IN
     1EQUILIBRIUM WITH THE INITIAL LIQUID PHASE CONCENTRATION"
      PRINT*,"VOL       = ",VOL," CM**3 = LIQUID VOLUME"
      PRINT*,"CMASS     = ",CMASS," GRAMS = ACTIVATED CARBON MASS"
      PRINT*,"RHOC      = ",RHOC," GM/CM**3 = ACTIVATED CARBON PARTICLE DE
     1NSITY"
      PRINT*,"EQ1       = ",EQ1," GM/GM/((GM/CM**3)**EQ2) = THE COEFFICIEN
     1T OF THE FREUNDLICH ISOTHERM EQUATION"
      PRINT*,"EQ2       = ",EQ2," GM/GM/((GM/CM**3)**EQ2) = THE COEFFICIEN
     1T OF THE FREUNDLICH ISOTHERM EQUATION"
      PRINT*,"EEQ1      = ",EEQ1," DIMENSIONLESS = THE EXPONENT OF THE FRE
     1UNDLICH ISOTHERM"
      PRINT*,"EEQ2      = ",EEQ2," DIMENSIONLESS = THE EXPONENT OF THE FRE
     1UNDLICH ISOTHERM"
      PRINT*,"CEP       = ",CEP
      PRINT*,"EQ1P      = ",EQ1P
      PRINT*,"EEQ1P     = ",EEQ1P
      PRINT*,"FQUE      = ",FQUE
      PRINT*,"QUP1      = ",QUP1
      PRINT*,"R         = ",R," CM = RADIUS OF ACTIVATED CARBON PARTICLES"
      PRINT*,"DS1       = ",DS1," CM**2/SEC = THE SURFACE DIFFUSION "
     2"COEFFICIENT"
      PRINT*,"DS2       = ",DS2," CM**2/SEC = THE SURFACE DIFFUSION "
     1"COEFFICIENT"
      PRINT*,"KF1       = ",KF1," CM/SEC = EXTERNAL LIQUID FILM TRANSFER "
     1"COEFFICIENT"
      PRINT*,"KF2       = ",KF2," CM/SEC = EXTERNAL LIQUID FILM TRANSFER "
     1"COEFFICIENT"
      PRINT*,"KB1       = ",KB1," (1./SEC) = MICROPORE RATE COEFFICIENT"
      PRINT*,"KB2       = ",KB2," (1./SEC) = MICROPORE RATE COEFFICIENT"
      PRINT*,"F1        = ",F1
      PRINT*,"F2        = ",F2
      PRINT*,"DS12      = ",DS12
      PRINT*,"DS21      = ",DS21
      PRINT*,"KB12      = ",KB12
      PRINT*,"KB21      = ",KB21
      PRINT*,"TT        = ",TT," HOURS = TOTAL TIME"
      PRINT*,"DT        = ",DT," MIN. = DIFFERENTIAL TIME STEP SIZE"
      PRINT*,"DTT       = ",DTT," (MIN.) = INITIAL DIFF. TIME STEP"
      PRINT*,"BIGF1     = ",BIGF1
      PRINT*,"BIGF2     = ",BIGF2

      PRINT*,"NOB       = ",NOB," = NUMBER OF OBSERVATIONS"
      PRINT*,"N         = ",N1," = NUMBER OF O.D.E.'S BEING SOLVED"
      PRINT*,"N2        = ",N2," = TWICE N1"
      PRINT*,"N1        = ",N1
      PRINT*,"NPROB     = ",NPROB," = PROBLEM NUMBER"
      PRINT*,"NP        = ",NP," =NUMBER OF PARAMETERS REGRESSED"
      PRINT*,"KDOT1     = ",KDOT1
      PRINT*,"KDOT2     = ",KDOT2
      PRINT*,"KDOT1P    = ",KDOT1P
      PRINT*,"MW1       = ",MW1
      PRINT*,"MW2       = ",MW2
      PRINT*,"ITMAX     = ",ITMAX
      PRINT*,"NSIG      = ",NSIG
      PRINT*,"NNN       = ",NNN
      PRINT*,"FAC1      = ",FAC1
      PRINT*,"FAC2      = ",FAC2
```

```
      NMIN=NMIN+1
      NCOL1=NCOL-NPIN
      NCOL2=2*NCOL
      NCOL3=NCOL2+1
      NCOL4=NCOL3+NCOL
      NCOL5=NCOL4+NCOL
      NCOL6=NCOL5+1
      NCOL1P=NCOL+1
      NCOL3P=NCOL3+1
      NCOL2M=NCOL2-1
      NCOL5M=NCOL5-1
      NCOL1M=NCOL1-1
      PRINT*,"NCOL   = ",NCOL
      PRINT*,"NCOL1  = ",NCOL1
      PRINT*,"NCOL2  = ",NCOL2
      PRINT*,"NCOL3  = ",NCOL3
      PRINT*,"NCOL4  = ",NCOL4
      PRINT*,"NCOL5  = ",NCOL5
      PRINT*,"NCOL6  = ",NCOL6
      PRINT*,"NCOL1M = ",NCOL1M
      PRINT*,"NCOL1P = ",NCOL1P
      PRINT*,"NCOL2M = ",NCOL2M
      PRINT*,"NCOL3P = ",NCOL3P
      PRINT*,"NCOL5M = ",NCOL5M
      WRITE(6,127)
  127 FORMAT("1 /////" ,10X," THE VALUES OF PAR(I)"/)
      PRINT*,"PAR(1-7) = ",(PAR(IOP),IOP=1,7)
      PRINT*,"PAR(8-14) = ",(PAR(IOP),IOP=8,14)
      PRINT*,"PAR(15-21) = ",(PAR(IOP),IOP=15,21)
      PRINT*,"PAR(22-28) = ",(PAR(IOP),IOP=22,28)
      M11=M1+1
      PRINT*,"CS1OLD   = ",CS1OLD
      PRINT*,"CS2OLD   = ",CS2OLD
      WRITE(6,322)
  322 FORMAT("1",5X,"CALCULATIONS OF QS FOR GIVEN VALUES OF CS"//" ",2X
     1,"CS1MOL",10X,"CS2MOL",10X,"CS1",10X,"CS2",10X,"QS1MOL",10X,"QS2MOL"
     2,10X,"CS1",10X,"CS2",10X,"QS1",10X,"QS2")
      DO 333 I=5,15
       CS1=CS2=10.**(-I)
       G(1)=CS1*C01/MW1
       G(2)=CS2*C02/MW2
```

```
   SUBROUTINE READIN     73/730  OPT=2                    FTN 4.8+587        85/07/25
       TERM = (((PAR(15)*G(1)**PAR(3) + PAR(16)*G(2)**PAR(4))
      1        ** PAR(22)) ** PAR(11))
       QS1MOL= PAR(1)*G(1)**PAR(3)
      1        + TERM*(((PAR(18)*G(1)**PAR(3))
      2        ** PAR(22)) ** PAR(27)
       QS2MOL= PAR(2)*G(2)**PAR(4)
      1        + TERM*(((PAR(19)*G(2)**PAR(4))
      2        ** PAR(22)) ** PAR(27)
       QS2=QS2MOL*MW2/Q02
       QS1=QS1MOL*MW1/Q01
       WRITE(6,355) G(1),G(2),QS1MOL,QS2MOL,CS1,CS2,QS1,QS2
  333  CONTINUE
  355 FORMAT(" ",3X,8(1X,E14.6))
       CS1=CS1OLD
       CS2=CS2OLD
       G(1)=CS1*C01/MW1
       G(2)=CS2*C02/MW2
       TERM = (((PAR(15)*G(1)**PAR(3) + PAR(16)*G(2)**PAR(4))
      1        ** PAR(22)) ** PAR(11))
       QS1MOL= PAR(1)*G(1)**PAR(3)
      1        + TERM*(((PAR(18)*G(1)**PAR(3))
      2        ** PAR(22)) ** PAR(27)
       QS2MOL= PAR(2)*G(2)**PAR(4)
      1        + TERM*(((PAR(19)*G(2)**PAR(4))
      2        ** PAR(22)) ** PAR(27)
       YT(NCOL5)=QS2MOL*MW2/Q02
       YT(NCOL2)=QS1MOL*MW1/Q01
       CS1OLD=CS1*C01/MW1
       CS2OLD=CS2*C02/MW2
       WRITE(6,128)
  128 FORMAT("1",
      1/)
       PRINT*,"Y(1 TO N1) = ",(YT(I),I=1,N1)
       PRINT*,"Y(N11 TO N2) = ",(YT(I),I=N11,N2)
       WRITE(6,16)
   16 FORMAT("1",20X,"CONCENTRATIONS",23X,"REDUCED CONC."/" ",
      110X,"TIME",29X,"TIME"/" ",
      119X,"COMP. 01",2X,"COMP. 02",10X,"COMP. 01",
      2 2X,"COMP. 02"/" ",5X,"(MIN.)",6X,"(MG/L)",5X,"(MG/L)",6X,
      3"(SEC.)"//)
       DO 20 J=1,NOB
       READ(5,*) XMIN(J),COBS1(J),COBS2(J),TSEC(J)
       XO1(J)=COBS1(J)/(C01*1.E+6)
       XO2(J)=COBS2(J)/(C02*1.E+6)
       RT(J)=TSEC(J)+XMIN(J)*60.0
       WRITE(6,38) J,XMIN(J),COBS1(J),COBS2(J),TSEC(J),XO1(J),XO2(J)
   20  CONTINUE
   38 FORMAT(" ",I3,5X,F7.0,3X,F7.3,2X,F9.5,2X,F10.0,2X,F12.6,2X,F12.6
      1)
       WRITE(6,1000)
 1000   FORMAT(1H1//" PROGRAM ACKINE OUTPUT"///)
       RETURN
       END
```

```
      SUBROUTINE MODEL(NOB,MPROB,TH,CC1,CC2,NOG,MP)
      DIMENSION Y(26),YPRIME(26)
      DIMENSION TH(8),TRT(100),CC1(110),CC2(110),PRT(110)
      DIMENSION WWK(286), IKWK(26)
      REAL KB1,KB2,KF1,KF2,MW1,MW2,KB12,KB21
      REAL KDOT1,KDOT1P,KDOT2
      EXTERNAL FCNOW
      EXTERNAL FCNJ
      COMMON /AT1/ CMASS,VOL,R,RHOC,FCON
      COMMON /IT1/ DS1,DS2,KF1,KF2,KB1,KB2,F1,F2,BIGF1,BIGF2
      COMMON /IT2/ CON1,CON2,COR1,COR2,COB1,COB2,COM1,COM2,CDS
      COMMON /IT4/ N1,N2,MS1,MS2,M11,MMIN
      COMMON /IT5/ TT,DT,DTT
      COMMON /IT7/ W11,W12,W21,W22,W31,W32
      COMMON /IT8/CO1,CO2,Q01,Q02,MW1,MW2,FQUE,HKEY,XKEY
      COMMON /IT9/ AQ,AQP,BQ
      COMMON /IT10/ KDOT1,KDOT1P,KDOT2,EEQ1I,EEQ1PI,EEQ2I,QUP1
      COMMON /AT6/ N
      COMMON /AT7/ TSEC(110),XMIN(110)
      COMMON /AT8/ XD1(110),XD2(110)
      COMMON /AT9/ YY(26)
      COMMON /AT10/ RT(100)
      COMMON /TON/ CS1OLD,CS2OLD,CS1,CS2,XTK1,XTK2
      COMMON /PON/ MSIG,MNNM,ITMAX,PAR(30)
      COMMON /BT7/ TOL, METH, MITER, MSTART
      COMMON /GEAR/ RUMMY(48) ,KDUMMY(6), IRUMMY(36)
      COMMON /XA/ A(10,10) , B(10,10) , W(10)
      COMMON /CROSS/ DS12,DS21,KB12,KB21
      COMMON /NC/ NCOL,NCOL1,NCOL2,NCOL3,NCOL4,NCOL5,NCOL6,NCOL1P
     1,NCOL3P,NCOL2M,NCOL5P,NCOL1M
      COMMON /ZAP/ CON12,CON21,COB12,COB21
      COMMON /DAVID/ CDS12, CDS22, CDS21
      DS1=TH(1)
      KB1=TH(2)
      F1=TH(3)
      KF1=TH(4)
      DS2=TH(5)
      KB2=TH(6)
      F2=TH(7)
      KF2=TH(8)
      PRINT*,'IN MODEL: DS1=',DS1,' KB1=',KB1,' F1=',F1,' KF1=',KF1
      PRINT*,'IN MODEL: DS2=',DS2,' KB2=',KB2,' F2=',F2,' KF2=',KF2
      TF=DS1/R**2
      XKEY=HKEY*3600.*TF
      XTK1M=0.9*XKEY
      XTK1=0.98*XKEY
      XTK2=1.02*XKEY
      XTK2M=1.1*XKEY
      H=DT*TF*60.0
      DO 17 JT=1,NOG
   17 TRT(JT)=RT(JT)*TF
      DO 18 JIN=1,N
   18 Y(JIN)=YY(JIN)
      DO 19 LIP=1,NOB
   19 PRT(LIP)=TSEC(LIP)*TF
      CDS=DS2/DS1
      FF1=1.-F1
      FF2=1.-F2
      BIGF1=-CMASS/(VOL*RHOC)
      IF(F1.EQ.1.000) FF1=1.00
      IF(F2.EQ.1.000) FF2=1.00
      PRINT*,'FF1    = ',FF1
      PRINT*,'FF2    = ',FF2
      PRINT*,'TF     = ',TF
      PRINT*,'FF1    = ',FF1
      PRINT*,'XKEY   = ',XKEY
      PRINT*,'XTK1M  = ',XTK1M
      PRINT*,'XTK1   = ',XTK1
      PRINT*,'XTK2   = ',XTK2
      PRINT*,'XTK2M  = ',XTK2M
      PRINT*,'CDS    = ',CDS
      CON1=BIGF1*KF1*R/DS1/F1
      CON2=(BIGF2*KF2*R/DS2/F2)*CDS
      COM1=KB1*R*R/DS1/F1
      COM2=KB2*R*R/DS1/F2
      COB1=KB1*R*R/FF1/DS1
      COB2=KB2*R*R/FF2/DS1
      COM12=KB12*R*R/DS1/F1
      COM21=KB21*R*R/DS1/F2
      COB12=KB12*R*R/DS1/FF1
      COB21=KB21*R*R/DS1/FF2
      COR1=FF1*.5*KF1*R/DS1
      COR2=FF1*.5*KF2*R/DS1
      CDS12=DS12*Q02 / (DS1*Q01)
      CDS21=DS21*Q01 / (DS1*Q02)
      CDS22=DS2 / DS1
      PRINT*,'CON1   = ',CON1
      PRINT*,'CON2   = ',CON2
      PRINT*,'COB1   = ',COB1
      PRINT*,'COB2   = ',COB2
      PRINT*,'COM1   = ',COM1
      PRINT*,'COM2   = ',COM2
      PRINT*,'COR1   = ',COR1
      PRINT*,'COR2   = ',COR2
      PRINT*,'COM21  = ',COM21
      PRINT*,'COM12  = ',COM12
      PRINT*,'COB12  = ',COB12
      PRINT*,'COB21  = ',COB21
      PRINT*,'CDS12  = ',CDS12
      PRINT*,'CDS21  = ',CDS21
      PRINT*,'CDS22  = ',CDS22
      DXS=DTT*60.0*TF
      PRINT*,'DXS    = ',DXS
      DXOLD=DXS
      DXOLD=DXOLD
      X=0.0
      INDEX = 1
      SUM=0.0
```

```
C*****************************************************************C
C                                                                 C
      H = TRT(1) / HSTART
      KP=1
      DO 67 K=1,NOG
   61 XEND = TRT(K)
      IF(KP.GT.NOB) GO TO 62
      IF(TRT(K).LE.PRT(KP)) GO TO 62
      XEND=PRT(KP)
      IFOC=1
   62 CONTINUE
      T = X / TF / 60.
      PRINT*,"BEFORE DGEAR , T=",T," X=",X," XEND=",XEND," TRT(K)="
     1,TRT(K)," Y(N1)=",Y(N1)," Y(N2)=",Y(N2)
      WRITE(6,65) Y(NCOL2),Y(11),Y(12),Y(13)
   65 FORMAT(" ",30X,"Y(NCOL2)=",E16.7," Y(11 TO 13)=",3(E16.7,1X))
      PRINT*," TOL=",TOL," METH=",METH," MITER=",MITER,
     +" INDEX=",INDEX," N=",N," IER=",IER," H=",H," K=",K," KP="
     +,KP
   64 CONTINUE
      CALL DGEAR(N,FCNOH,FCNJ,X,H,Y,XEND,TOL,METH,MITER,
     1  INDEX,IKNK,WWK,IER)
      IF(IER.GT.128) GO TO 120
      IF(IFOC.NE.1) GO TO 66
      SUM=SUM+((Y(N1)-XD1(KP))**2)+((Y(N2)-XD2(KP))**2)
      IFOC=0
      KP=KP+1
      GO TO 61
   66 CONTINUE
      T=X/TF/60.
      XMINN=XMIN(K)=T
      CC1(K)=Y(N1)
      CC2(K)=Y(N2)
      PRINT*,"K = ",K," CC1(K) = ",CC1(K)," CC2(K) = ",CC2(K)," T=",T
     1," X=",X," TRT(K)=",TRT(K)
   67 CONTINUE
      PRINT*,"END OF MODEL, DS12=",DS12," DS21=",DS21," SUM=",SUM
      PRINT*,"KSTEPS= ",IRUNNY(7)
      RETURN
  120 PRINT*,"     TROUBLE --"," K= ",K," IER= ",IER
      RETURN
      END
```

```
      SUBROUTINE FCNISO(G,F,N,PAR)
      INTEGER N
      REAL G(N),F(N),PAR(30)
      IF(G(1).GT.0.0.AND.G(2).GT.0.0) GO TO 5
      IF(G(1).LT.0.0) F(1)=(1.0E20)*ABS(G(1))
      IF(G(2).LT.0.0) F(2)=(1.0E20)*ABS(G(2))
      GO TO 40
    5 CONTINUE
      IF(G(1).GT.PAR(14)) GO TO 20
      TERM = (((PAR(15)*G(1)**PAR(3) + PAR(16)*G(2)**PAR(4))
     1      ** PAR(22)) ** PAR(11))
      F(1) = PAR(8) - PAR(1)*G(1)**PAR(3)
     1       - TERM*((PAR(18)*G(1)**PAR(3))
     2       ** PAR(22)) * PAR(27)
      F(2) = PAR(9) - PAR(2)*G(2)**PAR(4)
     1       - TERM*((PAR(19)*G(2)**PAR(4))
     2       ** PAR(22)) * PAR(27)
      GO TO 40
C
   20 TERM = (((PAR(17)*G(1)**PAR(7) + PAR(26)*G(2)**PAR(4))
     1      ** PAR(23)) ** PAR(13))
      F(1) = PAR(8) - PAR(10)*G(1)**PAR(7)
     1       - TERM*((PAR(12)*G(1)**PAR(7))
     2       ** PAR(23)) * PAR(28)
      F(2) = PAR(9) - PAR(2)*G(2)**PAR(4)
     1       - TERM*((PAR(19)*G(2)**PAR(4))
     2       ** PAR(23)) * PAR(28)
C
   40 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE FCNON(N,X,Y,YPRIME)
      REAL  NURRY,NZRRY
      REAL Y(N),YPRIME(N),X
      REAL G(2),WK(300)
      REAL KB1,KB2,KF1,KF2,MW1,MW2
      REAL KDOT1,KDOTIP,KDOTZ
      COMMON /AT1/ CMASS,VOL,R,RHOC,FCON
      COMMON /ZT1/ CS1,CS2,KF1,KF2,KB1,KB2,F1,F2,BIGF1,BIGF2
      COMMON /ZT2/ CON1,CON2,COR1,COR2,COB1,COB2,COM1,COM2,COS
      COMMON /ZT4/ M1,M2,MS1,MS2,ML1,MMIN
      COMMON /ZT5/ TT,DT,DTT
      COMMON /ZT7/ MI1,MI2,MZ1,MZ2,MJ1,MJ2
      COMMON /ZT8/CB1,CB2,B01,B02,MW1,MW2,FQUE,NKEY,XKEY
      COMMON /ZT10/ KDOT1,KDOTIP,KDOT2,EEQ1I,EEQ1PI,EEQ2I,QUP1
      COMMON /POW/ NSIG,NMN,ITMAX,PAR(30)
      COMMON /TOW/ CS1OLD,CS2OLD,CS1,CS2,XTK1,XTK2
      COMMON /XA/ A(10,10), B(10,10), MI(10)
      COMMON /MC/ NCOL,NCOL1,NCOL2,NCOL3,NCOL4,NCOL5,NCOL6,NCOL1P
     1,NCOL3P,NCOLZM,NCOL5M,NCOL1M
      COMMON /ZAP/ COM12,COM21,COB12,COB21
      COMMON /DAVID/ COS12, COS22, COS21
      EXTERNAL FCNISO
      IF(X.GE.XKEY) GO TO 20
      IF(Y(NCOL2).LE.QUP1) CS1=FQUE*Y(NCOL2)**EEQ1I
      IF(Y(NCOL2).GT.QUP1) CS1=Y(NCOL2)**EEQ1PI
      CS2=Y(NCOL5)**EEQ2I
      CS1OLD=CS1*CB1/MW1
      CS2OLD=CS2*CB2/MW2
      GO TO 30
   20 CONTINUE
      PAR(8)=Y(NCOL2)*B01/MW1
      PAR(9)=Y(NCOL5)*B02/MW2
      G(1)=CS1OLD
      G(2)=CS2OLD
      CALL ZSPCW(FCNISO,NSIG,NMN,ITMAX,PAR,G,FNORM,WK,IER)
      IF(IER.NE.0) PRINT*,'IER=',IER,' FNORM=',FNORM,' G(1)=',G(1),
     1' G(2)=',G(2)
      CS1OLD=G(1)
      CS2OLD=G(2)
      CS1=G(1)*MW1/CB1
      CS2=G(2)*MW2/CB2
   30 CONTINUE
C
      DO 50 JT=1,NCOL
      NEXT = NCOL+JT
      NJT = NCOL3+JT
      NNEXT = NJT+NCOL
      YPRIME(JT) = COB1*(Y(NEXT)-Y(JT)) + COB12*(Y(NNEXT)-Y(NJT))
   50 YPRIME(NJT) = COB2*(Y(NNEXT)-Y(NJT)) + COB21*(Y(NEXT)-Y(JT))
C
      DO 51 JU=NCOL1P,NCOLZM
      NOWP = JU-NCOL
      NJU = NCOL3+JU
      NNOWP = NJU-NCOL
      YPRIME(JU) = 0.0
      YPRIME(NJU) = 0.0
      DO 52 JV=NCOL1P,NCOLZ
      JVV = JV-NCOL
      NJV = NCOL3+JV
      NJVV = NCOL3+JVV
      YPRIME(JU) = YPRIME(JU) + B(NOWP,JVV)*Y(JV)
     1           + COS12*B(NOWP,JVV)*Y(NJV)
      YPRIME(NJU) = YPRIME(NJU) + COS22*B(NOWP,JVV)*Y(NJV)
     1            + COS21*B(NOWP,JVV)*Y(JV)
   52 CONTINUE
      YPRIME(JU) = YPRIME(JU) - CON1*(Y(JU)-Y(NOWP))
     1           - COM12*(Y(NJU)-Y(NNOWP))
      YPRIME(NJU) = YPRIME(NJU) - COM2*(Y(NJU)-Y(NNOWP))
     1            - COM21*(Y(JU)-Y(NOWP))
   51 CONTINUE
C
      YPRIME(NCOL2) = COM1*(Y(NCOL3)-CS1)
      YPRIME(NCOL5) = COM2*(Y(NCOL6)-CS2)
C
      DO 79 KAT=1,NCOL
      KOT = KAT+NMIN
      NKAT = NCOL3+KAT
      NKOT = NCOL3+KOT
      YPRIME(NCOL2)=YPRIME(NCOL2) - M(KAT)*CON1*(Y(KOT)-Y(KAT))
     1             - M(KAT)*COM12*(Y(NKOT)-Y(NKAT))
      YPRIME(NCOL5) = YPRIME(NCOL5) - M(KAT)*COM2*(Y(NKOT)-Y(NKAT))
     1              - M(KAT)*COM21*(Y(KOT)-Y(KAT))
   79 CONTINUE
C
      NURRY = NZRRY = 0.0
C
      DO 80 KORT=1,NCOL1M
      KART = KORT+NCOL
      NKORT = NCOL3+KORT
      NKART = NCOL3+KART
      NURRY = NURRY+YPRIME(KART)*M(KORT)
      NZRRY = NZRRY+YPRIME(NKART)*M(KORT)
   80 CONTINUE
C
      YPRIME(NCOL2) = (1./M(NCOL1))*(YPRIME(NCOL2)-NURRY)
      YPRIME(NCOL5) = (1./M(NCOL1))*(YPRIME(NCOL5)-NZRRY)
      YPRIME(NCOL3) = COR1*(Y(NCOL3)-CS1)
      YPRIME(NCOL6) = COR2*(Y(NCOL6)-CS2)
      RETURN
      END
```

APPENDIX G1

1,1,2-TRICHLOROETHANE BATCH KINETICS DATA

Initial Concentration = 567 µg/ℓ
Carbon Dosage: Mean = 0.04288 g/ℓ σ = 0.000128 (0.3 %)

I	MINUTES	CONCENTRATION (MICROG/L)	REDUCED CONCEN.	TIME (SEC.)
1	22.0	.510900	.901217	1320.0
2	39.0	.496700	.876169	2352.0
3	55.0	.480600	.847769	3294.0
4	64.0	.461900	.814782	3852.0
5	83.0	.473700	.835597	5012.0
6	98.0	.470900	.830658	5869.0
7	132.0	.426100	.751632	7920.0
8	153.0	.406800	.717587	9165.0
9	187.0	.414100	.730464	11245.0
10	223.0	.382800	.675251	13374.0
11	241.0	.367100	.647557	14478.0
12	274.0	.349900	.617216	16457.0
13	310.0	.342800	.604692	18910.0
14	330.0	.320700	.565708	19783.0
15	352.0	.363900	.641912	21116.0
16	391.0	.321800	.567649	23443.0
17	423.0	.317950	.560857	25418.0
18	450.0	.310500	.547716	27389.0
19	479.0	.306900	.541365	28765.0
20	511.0	.286500	.505380	30664.0
21	542.0	.311900	.550185	32507.0
22	1229.0	.211000	.372200	73718.0
23	1469.0	.193400	.341154	88132.0
24	1675.0	.183100	.322985	100529.0
25	2759.0	.160680	.283436	165562.0
26	3058.0	.158766	.280060	183505.0
27	4199.0	.148570	.262074	251962.0
28	4611.0	.143240	.252672	276651.0
29	5683.0	.142050	.250573	340966.0
30	5756.0	.140580	.247980	345373.0
31	7096.0	.143590	.253290	425748.0
32	7356.0	.142990	.252231	441384.0
33	7703.0	.137390	.242353	462196.0
34	8680.0	.128400	.226495	520781.0
35	9015.0	.138500	.244311	540916.0
36	10270.0	.137000	.241665	616225.0
37	10406.0	.129700	.228788	624373.0
38	11351.0	.137200	.242018	681073.0
39	11416.0	.142200	.250838	684952.0
40	14383.0	.139700	.246428	862981.0
41	15717.0	.127530	.224960	943032.0
42	18835.0	.132420	.233586	1130105.0
43	21607.0	.134540	.237326	1296435.0
44	24367.0	.130450	.230111	1462020.0
45	24386.0	.133900	.236197	1463204.0

APPENDIX G2

FAUQUIER RIVER WATER BATCH KINETICS DATA

Initial Concentration = 4.827 mg TOC/ℓ (Mean of 5 controls)
Carbon Dosage: Mean = 0.04691 g/ℓ
σ = 0.00014 (0.3 %)

I	MINUTES	CONCENTRATION (MICROG/L)	REDUCED CONCEN.	TIME (SEC.)
1	20.0	4.823000	.999171	1196.0
2	28.0	4.775000	.989227	1714.0
3	39.0	4.823000	.999171	2347.0
4	49.0	4.775000	.989227	2952.0
5	60.0	4.814000	.997307	3600.0
6	82.0	4.756000	.985291	4940.0
7	151.0	4.736000	.981148	9049.0
8	180.0	4.649000	.963124	10814.0
9	211.0	4.659000	.965196	12680.0
10	241.0	4.630000	.959188	14483.0
11	276.0	4.678000	.969132	16531.0
12	299.0	4.601000	.953180	17960.0
13	329.0	4.639000	.961052	19747.0
14	360.0	4.601000	.953180	21574.0
15	391.0	4.581000	.949037	23480.0
16	420.0	4.562000	.945100	25229.0
17	449.0	4.523000	.937021	26966.0
18	480.0	4.562000	.945100	28818.0
19	540.0	4.775000	.989227	32404.0
20	720.0	4.349000	.900974	43177.0
21	994.0	4.407000	.912989	59641.0
22	1185.0	4.398000	.911125	71133.0
23	1365.0	4.349000	.900974	81936.0
24	1602.0	4.330000	.897037	96134.0
25	2347.0	4.214000	.873006	140873.0
26	2693.0	4.194000	.868863	161554.0
27	3350.0	4.136000	.856847	200983.0
28	3836.0	4.039000	.836752	230168.0
29	4644.0	4.039000	.836752	278634.0
30	5261.0	3.952000	.818728	315684.0
31	6164.0	3.923000	.812720	366811.0
32	6838.0	3.827000	.792832	410258.0
33	7645.0	3.865000	.800704	458686.0
34	7645.0	3.730000	.772737	458686.0
35	7646.0	3.827000	.792832	458734.0
36	7646.0	3.827000	.792832	458769.0
37	15655.0	3.420000	.708515	939355.0
38	18557.0	3.275000	.678475	1113432.0
39	21741.0	3.227000	.668531	1304472.0

APPENDIX G3

BISOLUTE BATCH KINETICS DATA

Initial Concentration

TOC 4.536 mg TOC/ℓ

TCEA 555.4 µg TCEA/ℓ

Carbon Dosage: Mean = 0.06241 g/ℓ

σ = 0.00015 (0.24 %)

	CONCENTRATIONS			REDUCED CONC.		
	TIME (MIN.)	COMP. #1 (MG/L)	COMP. #2 (MG/L)	TIME (SEC.)	COMP. #1	COMP. #2
1	35.	4.450	.47230	2122.	.992971	.850378
2	47.	4.430	.46090	2822.	.988508	.829852
3	57.	4.410	.46220	3474.	.984046	.832193
4	71.	4.371	.43390	4316.	.975343	.781259
5	91.	4.371	.42740	5477.	.975343	.769535
6	122.	4.410	.40980	7355.	.984046	.737847
7	153.	4.371	.37620	9235.	.975343	.677350
8	188.	4.292	.33870	11329.	.957715	.609831
9	212.	4.273	.34940	12723.	.953475	.629096
10	278.	4.243	.31930	16709.	.946781	.574901
11	326.	4.253	.29420	19585.	.949013	.529708
12	361.	4.194	.29570	21677.	.935847	.532409
13	392.	4.224	.27570	23567.	.942542	.496399
14	422.	4.165	.25530	25358.	.929376	.459669
15	451.	4.174	.25620	27115.	.931385	.461289
16	477.	4.135	.26010	28628.	.922682	.468311
17	513.	4.096	.25400	30804.	.913980	.457328
18	546.	4.108	.24540	32803.	.916211	.441844
19	1319.	3.958	.17184	79168.	.883186	.309399
20	1684.	3.880	.15160	101067.	.865782	.272956
21	1846.	3.811	.15041	110937.	.850385	.270796
22	2755.	3.585	.12540	165305.	.799955	.225783
23	2995.	3.614	.13220	179715.	.806426	.238135
24	3233.	3.585	.12890	194018.	.799955	.232085
25	4232.	3.487	.12260	253977.	.778088	.220742
26	5697.	3.339	.12420	341834.	.745063	.223623
27	7207.	3.211	.12410	432436.	.716501	.223443
28	8821.	3.113	.10770	529269.	.694633	.193914
29	10162.	3.094	.11960	609761.	.690394	.215340
30	11770.	2.897	.12290	706248.	.646435	.221282
31	13032.	2.956	.12520	781949.	.659681	.225423
32	14362.	2.956	.12360	861741.	.659681	.222542
33	15892.	2.897	.11860	953559.	.646435	.213540
34	21528.	2.641	.12336	1291692.	.589312	.222110
35	23288.	2.543	.12114	1397339.	.567444	.218113
36	24369.	2.543	.12514	1462157.	.567444	.225515
37	26023.	2.504	.11914	1561385.	.558741	.214512

APPENDIX HI

LISTING OF THE COMPUTER PROGRAM BASED ON THE RAZZAGHI MODEL FOR BISOLUTE ADSORPTION ISOTHERMS

The Razzaghi model was calibrated using the computer program RAZZ10 which is listed below. RAZZ10 uses the Razzaghi competitive isotherm equations for the two components coupled with their respective mass balances. These non linear equations are solved simultaneously by the IMSL (1982) routine ZSPOW, which is based on Newton's method with finite difference approximations for the partial derivatives.

The program RAZZ10 uses the routien MVEST to conduct the parameter estimation for the multiresponse experimental data. MVEST was developed by Jutan (1976) who includes a listing of the routine in his report. The program also uses subroutine ISOPLOT for plotting, which was not included in the listing as it is dependent on the computing systems at McMaster.

```
PROGRAM RAZZ18     73/738  OPT=2                          FTN 4.8+587          85/07/25
      1            PROGRAM RAZZ18(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
                   DIMENSION CF1(31),CF2(31),QQ(31),Q92(31),Q1CXP(31),Q2EXP(31)
                   DIMENSION C1EXP(31),C2EXP(31),VEXP(31),VMEXP(31),VMF(31)
      5            DIMENSION CL1(100),CL2(100),QL1(100),QL2(100),VML(100)
                   DIMENSION CF2(31),QQQ(31)
                   DIMENSION BETA(9),V(2,31),XX(3,31),PM(2,31,3),A1(2,31),A(2,31)
                  1,P(2,31)
                   DIMENSION C1IN(31),C2IN(31)
                   DIMENSION PAR(31),X(11),XC1(31,11),XC2(31,11),XVM(31,11)
     10            DIMENSION TH(5),NK(500)
                   REAL MEXP(31)
                   INTEGER NUN(31)
                   REAL K1,KK1,K2,KK2,MW1,MW2,N1,N2
     15            REAL KK1P,KK2P,K1P,K2P,N1P,N2P
                   INTEGER TEST(4),COMP1(4),COMP2(4)
                   COMMON /POW/ NSIG,N,ITMAX,PORE(31),FAC1,FAC2,Z1
                   EXTERNAL FCN,FCN1,FCN2,MODEL
                C
     20         C*****************************************************************
                C
                C        R A Z Z 1 8
                C
                C*****************************************************************
     25         C*****************************************************************
                C                                                                  C
                C        PROGRAM THAT REGRESSES THE COMPETITIVE ADSORPTION ISOTHERM C
                C        DATA TO THE RAZZAGHI COMPETITIVE ISOTHERM MODEL            C
     30         C                                                                  C
                C*****************************************************************
                C*****************************************************************
                C
     35         C     ASSUMPTIONS
                C                  1) THE ADSORPTION ISOTHERM OF BOTH COMPONENTS CAN BE
                C                     DESCRIBED BY FREUNDLICH ISOTHERM MODELS
                C                  2) ALL THOSE ASSUMPTIONS INHERENT WITH THE
     40         C                     RAZZAGHI COMPETITIVE ISOTHERM MODEL
                C                  3) ALL THOSE ASSUMPTIONS INHERENT WITH USING THE
                C                     IMSL ROUTINE "ISPOW" (IT SOLVES SIMULTANEOUS
                C                     NON-LINEAR EQUATIONS USING A MODIFIED NEWTON'S
     45         C                     METHOD)
                C*****************************************************************
                C
                C     DEVELOPED BY R.N. NAZBAITZ AT MCMASTER UNIV. IN MARCH 1985
     50         C*****************************************************************
                C
                      NN=2
                      READ(5,*) ITMAX,NSIG,NP
                      READ(5,20)TEST
     55            20  FORMAT(4(A10))
                      READ(5,20) COMP1
                      READ(5,20) COMP2
                      READ(5,*)C1INN,C2INN
```

```
PROGRAM RAZZ18     73/738  OPT=2                          FTN 4.8+587          85/07/25
                      READ(5,*) MW1,MW2,KK1,KK2,N1,N2,CFNON1
     60               READ(5,*) CC1P,CC2P,KK1P,KK2P,N1P,N2P
                      READ(5,*) QM1M,QM2M,BB1,BB2,CLNON1
                      READ(5,*)CCQ1P,CCQ2P,QM1MP,QM2MP,BB1P,BB2P
                      READ(5,*) NDATA,NO,NI,NPAR
                      READ(5,*)(BETA(I),I=1,NPAR)
     65               READ(5,*) MAXIT,EPS1,NFIG
                      READ(5,*) RLAM,FACT,RLMAX,RLMIN
                      READ(5,*) FAC1,FAC2,Z1
                      MW1=BETA(1)

     70                CC1IN = C1INN / MW1
                       CC2IN = C2INN / MW2
                      QM1=QM1M/MW1
                      B1=BB1*MW1
                      K2=KK2*(MW2)**(N2-1.)
     75               K2P=KK2P*(MW2)**(N2P-1.)
                      K1=KK1*(MW1)**(N1-1.)
                      K1P=KK1P*(MW1)**(N1P-1.)
                      C1P=CC1P/MW1
                      C2P=CC2P/MW2
     80               CQ1P=CCQ1P/MW1
                      CQ2P=CCQ2P/MW2
                      QM1P=QM1MP/MW1
                      QM2P=QM2MP/MW2
                      B1P=BB1P*MW1
     85               B2P=BB2P*MW2
                      CNON1F=CFNCN1/MW1
                      CNON1L=CLNON1/MW1
                      QM2=QM2M/MW2
                      B2=BB2*MW2
     90               PRINT*,'='
                      PRINT*,'=                NP = ',NP,' = NUMBER OF POINTS BEING CONSIDERED'
                     1    ' ALLOWED'      ITMAX = ',ITMAX,' = MAXIMUM NUMBER OF ITERATIONS',
```

```
      PRINT*,"        NSIG = ",NSIG," = NUMBER OF SIGNIFICANT DIGIT ",
     1"ACCURACY DESIRED"
      PRINT*,"         MW1 = ",MW1," = MOLECULAR WEIGHT OF COMPOUND # 1"
      PRINT*,"         MW2 = ",MW2," = MOLECULAR WEIGHT OF COMPOUND # 2"
      PRINT*,"      C1INM = ",C1INM," = INITIAL CONCENTRATION OF COMPOUND
     1 # 1 (MG/L)"
      PRINT*,"      C2INM = ",C2INM," = INITIAL CONCENTRATION OF COMPOUND
     1 # 2 (MG/L)"
      PRINT*,"FAC1    = ",FAC1
      PRINT*,"FAC2    = ",FAC2
      PRINT*,"Z1      = ",Z1
      PRINT*,"      NDATA = ",NDATA," = # OF DATA POINTS"
      PRINT*,"         NO = ",NO," = # OF DEPENDENT VARIABLES"
      PRINT*,"         NI = ",NI," = # OF INDEPENDENT VARIABLES"
      PRINT*,"       NPAR = ",NPAR," = # OF PARAMETERS REGRESSED"
      PRINT*,"       BETA = ",(BETA(I),I=1,NPAR)," THE INITIAL G",
     1"UESSES OF THESE PARAMETERS"
      PRINT*,"     MAXITR = ",MAXITR," MAX. # OF ITERATIONS ALLOWED"
     1," IN MARQUEST"
      PRINT*,"        DEL = ",DEL
      PRINT*,"       NFIG = ",NFIG
      PRINT*,"       RLAM = ",RLAM
      PRINT*,"       FACT = ",FACT


PROGRAM RAZZ10     73/730  OPT=2                    FTN 4.8+587      85/07/29

      PRINT*,"       RLMAX = ",RLMAX
      PRINT*,"       RLMIN = ",RLMIN
      WRITE(6,5010)
 5010 FORMAT("1",//////" ",2X," FREUNDLICH ISOTHERMS FOR THE FIRST "
     1,"COMPOUND ON A MASS BASIS"//)
      PRINT*,"         KK1 = ",KK1," = COEFFICIENT OF THE FREUNDLICH ADS
     1ORPTION ISOTHERM FOR COMPOUND # 1, IN TERMS OF MG/G"
      PRINT*,"        CC1P = ",CC1P," (MG/L) CONCENTRATION AT WHICH THE"
     1," SECOND FREUNDLICH ISOTHERM OF COMPOUND NO. 1 STARTS TO APPLY"
      PRINT*,"        KK1P = ",KK1P," COEFF. OF THE FREUNDLICH ISOTHERM ",
     1"( IN MGRAMS/GRAM) FOR THE SECOND RANGE OF COMPOUND NO.1"
      PRINT*,"         N1P = ",N1P," EXPONENT OF THE FREUNDLICH ISOTHERM",
     1" ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      WRITE(6,5020)
 5020 FORMAT("1",//////" ",2X," FREUNDLICH ISOTHERMS FOR THE SECOND ",
     1"COMPOUND ON A MASS BASIS")
      PRINT*,"         KK2 = ",KK2," = COEFFICIENT OF THE FREUNDLICH ADS
     1ORPTION ISOTHERM FOR COMPOUND # 2, IN TERMS OF MG/G"
      PRINT*,"         N2 = ",N2," = EXPONENT OF THE FREUNDLICH ADSORPT
     1ION ISOTHERM FOR COMPOUND # 2"
      PRINT*,"        CC2P = ",CC2P," (MG/L) CONCENTRATION AT WHICH THE ",
     1"SECOND FREUNDLICH ISOTHERM OF COMPOUND NO. 2 STARTS TO APPLY"
      PRINT*,"        KK2P = ",KK2P," COEFFICIENT OF THE FREUNDLICH ISOTHERM
     1 ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
      PRINT*,"         N2P = ",N2P," EXPONENT OF THE FREUNDLICH ISOTHERM",
     2" ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      WRITE(6,5030)
 5030 FORMAT("1",//////" ",2X,"THE LANGMUIR ISOTHERMS FOR THE FIRST ",
     1"COMPOUND ON A MASS BASIS"//)
      PRINT*,"       QM1N = ",QM1N," = COEFFICIENT OF THE LANGMUIR ADS
     1ORPTION ISOTHERM FOR COMPOUND # 1, IN TERMS OF MG/G"
      PRINT*,"        BB1 = ",BB1," = COEFFICIENT OF THE LANGMUIR"
     1," ISOTHERM , IN TERMS OF MG/G"
      PRINT*,"       CC1P = ",CC1P," (MG/L) CONCENTRATION AT WHICH THE ",
     1"SECOND LANGMUIR ISOTHERM OF COMPOUND NO. 1 STARTS TO APPLY"
      PRINT*,"      QM1NP = ",QM1NP," COEFFICIENT OF THE LANGMUIR ISOTHERM"
     1," ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      PRINT*,"       BB1P = ",BB1P," COEFFIENT OF THE LANGMUIR ISOTHERM"
     1," ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      WRITE(6,5040)
 5040 FORMAT("1",//////" ",2X," THE LANGMUIR ISOTHERMS FOR THE SECOND ",
     1"COMPOUND ON A MASS BASIS"//)
      PRINT*,"       QM2N = ",QM2N," = COEFFICIENT OF THE LANGMUIR ADS
     2ORPTION ISOTHERM FOR COMPOUND # 2, IN TERMS OF MG/G"
      PRINT*,"        BB2 = ",BB2," = COEFFICIENT OF THE LANGMUIR"
     1," ISOTHERM , IN TERMS OF MG/G"
      PRINT*,"       CC2P = ",CC2P," (MG/L) CONCENTRATION AT WHICH THE ",
     1"SECOND LANGMUIR ISOTHERM OF COMPOUND NO. 2 STARTS TO APPLY"
      PRINT*,"      QM2NP = ",QM2NP," COEFFICIENT OF THE LANGMUIR ISOTHERM"
     2," ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
      PRINT*,"       BB2P = ",BB2P," COEFFIENT OF THE LANGMUIR ISOTHERM"
     2," ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
      WRITE(6,5050)
 5050 FORMAT("1",//////" ",2X," THE FREUNDLICH ISOTHERMS FOR THE FIRST"
     1," COMPOUND ON A MOLAR BASIS"//)
      PRINT*,"        C1P = ",C1P," MOLAR CONCENTRATION AT WHICH THE"
     1," SECOND FREUNDLICH ISOTHERM OF COMPOUND NO. 1 STARTS TO APPLY"
      PRINT*,"         K1 = ",K1," = COEFFICIENT OF THE FREUNDLICH ADSO
     1RPTION ISOTHERM FOR COMPOUND # 1 , IN TERMS OF MMOLE/G"
      PRINT*,"         N1 = ",N1," = EXPONENT OF THE FREUNDLICH ADSORPT
     1ION ISOTHERM FOR COMPOUND # 1"
      PRINT*,"        K1P = ",K1P," COEFF. OF THE FREUNDLICH ISOTHERM ",
     1"( IN MMOLES/GRAM) FOR THE SECOND RANGE OF COMPOUND NO.1"
      PRINT*,"         N1P = ",N1P," EXPONENT OF THE FREUNDLICH ISOTHERM",
     1" ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      WRITE(6,5060)
 5060 FORMAT("1",//////" ",2X," THE FREUNDLICH ISOTHERMS FO THE SECOND",
     1" COMPOUND ON A MOLAR BASIS"//)
      PRINT*,"         K2 = ",K2," = COEFFICIENT OF THE FREUNDLICH ADSO
     1RPTION ISOTHERM FOR COMPOUND # 2 , IN TERMS OF MMOLE/G"
      PRINT*,"         N2 = ",N2," = EXPONENT OF THE FREUNDLICH ADSORPT
     1ION ISOTHERM FOR COMPOUND # 2"
```

```
      PRINT*,"     C2P = ",C2P," MOLAR CONCENTRATION AT WHICH THE "
     1"SECOND FREUNDLICH ISOTHERM OF COMPOUND NO.2 STARTS TO APPLY"
      PRINT*,"     K2P = ",K2P," COEFFICIENT OF THE FREUNDLICH ISOTHERM
     1" ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
      PRINT*,"     N2P = ",N2P," EXPONENT OF THE FREUNDLICH ISOTHERM",
     2" ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      WRITE(6,5070)
 5070 FORMAT(" "//////" ",2X," THE LANGMUIR ISOTHERMS FOR THE FIRST ",
     1"COMPOUND ON A MOLAR BASIS"//)
      PRINT*,"     C01P = ",C01P," MOLAR CONCENTRATION AT WHICH THE ",
     1"SECOND LANGMUIR ISOTHERM OF COMPOUND NO. 1 STARTS TO APPLY"
      PRINT*,"     QM1 = ",QM1," COEFFICIENT OF THE LANGMUIR ADSO
     1RPTION ISOTHERM FOR COMPOUND # 1 , IN TERMS OF MMOLE/G"
      PRINT*,"     B1 = ",B1," COEFFICIENT OF THE LANGMUIR ADSORP
     1TION ISOTHERM FOR COMPOUND # 1 , IN LITERS/MILLIMOLE"
      PRINT*,"     QM1P = ",QM1P," COEFFICIENT OF THE LANGMUIR ISOTHERM"
     1," ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      PRINT*,"     B1P = ",B1P," COEFFIENT OF THE LANGMUIR ISOTHERM"
     1," ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      WRITE(6,5080)
 5080 FORMAT(" "//////" ",2X," THE LANGMUIR ISOTHERM FOR COMPOUND #2 ",
     1"ON A MOLAR BASIS"//)
      PRINT*,"     C02P = ",C02P," MOLAR CONCENTRATION AT WHICH THE ",
     1"SECOND LANGMUIR ISOTHERM OF COMPOUND NO. 2 STARTS TO APPLY"
      PRINT*,"     B2 = ",B2," COEFFICIENT OF THE LANGMUIR ADSORP
     2TION ISOTHERM FOR COMPOUND # 2, IN LITERS/MILLIMOLE"
      PRINT*,"     QM2P = ",QM2P," COEFFICIENT OF THE LANGMUIR ISOTHERM"
     2," ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
      PRINT*,"     B2P = ",B2P," COEFFIENT OF THE LANGMUIR ISOTHERM"
     2," ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
      WRITE(6,5090)
 5090 FORMAT(" "/////////" ",2X,"THE VALUES OF PORE(I)"/)
      PORE(1)=KK1
      PORE(2)=K2
      PORE(3)=N1
      PORE(4)=N2
      PORE(5)=KK1P
      PORE(6)=K2P
      PORE(7)=N1P
      PORE(8)=N2P
      PORE(9)=CC1P-CFNON1
      PORE(10)=C2P
      PORE(11)=CFNON1
      PRINT*,"PORE (1 TO 7) =",(PORE(IG),IG=1,7)
      PRINT*,"PORE (8 TO 14)=",(PORE(IG),IG=8,14)
      DO 9500 J=1,NDATA
       READ*,C1EXP(J),C2EXP(J),Q1EXP(J),Q2EXP(J),MEXP(J),VEXP(J),NUN(J)
     1,C1IN(J),C2IN(J)
        PRINT*," "
       VMEXP(J)=VEXP(J)/MEXP(J)
       PRINT*,"C1EXP(J)=",C1EXP(J)," Q1EXP(J)=",Q1EXP(J)," C2EXP(J)=",
     1C2EXP(J)," Q2EXP(J)=",Q2EXP(J)," MEXP(J)=",MEXP(J)," VEXP(J)=",
     1VEXP(J)
 9500 CONTINUE
      WRITE(6,119)
      WRITE(6,120) TEST, COMP1, COMP2
      WRITE(6,125) C1INN, C2INN
      WRITE(6,230)
C
      DO 9250 I=1,NP
        WRITE(6,200) C1EXP(I),C2EXP(I),Q1EXP(I),Q2EXP(I),VMEXP(II
 9250 CONTINUE
      DO 500 J=1,NDATA
      C2EXP(J)=C2EXP(J)/MW2
      Q2EXP(J)=Q2EXP(J)/MW2
      C2IN(J)=C2IN(J)/MW2
      XX(3,J)=VMEXP(J)
      XX(1,J)=C1IN(J)-CFNON1
      XX(2,J)=C2IN(J)
      Y(1,J)=(C1EXP(J)-CFNON1)
      Y(2,J)=C2EXP(J)
  500 CONTINUE
      WRITE(6,119)
  119 FORMAT("1",10X,"EXPERIMENTAL DATA"/////)
      WRITE(6,120) TEST,COMP1,COMP2
  120 FORMAT("0",15X,"EXPERIMENT # ",4(A10)//"0",15X,"COMPONENT # 1 = ",
     14(A10)/"0",15X,"COMPONENT # 2 = ",4(A10)//)
      WRITE(6,125) CC1IN, CC2IN
  125 FORMAT(" INITIAL CONCENTRATION OF COMPUND # 1 = ",E14.6,
     2       " MILLIMOLE / L"/
     3       " INITIAL CONCENTRATION OF COMPOUND # 2 = ",E14.6,
     4       " MILLIMOLE / L"//)
      WRITE(6,130)
  130 FORMAT(" ",6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",
     1       " ",13X,"V/M",14X,"NUN"//
     1       " ",3X,"M-MOLE/L",11X,"M-MOLE/L",9X,"M-MOLE/G",9X,
     1       "M-MOLE/G",9X,"LITERS/G"/)
C
      DO 158 I=1,NDATA
      WRITE(6,140) C1EXP(I),C2EXP(I),Q1EXP(I),Q2EXP(I),VMEXP(I),NUN(I)
  140 FORMAT(" ",5(E14.6,3X),3X,I3)
  158 CONTINUE
      WRITE(6,5100)
 5100 FORMAT("1",3X,"INPUT TO MVEST"//" ",1X,"X(1,I)",5X,
     1"X(2,I)",5X,"X(3,I)",5X,"Y(1,I)",5X,"Y(2,I)"/)
      DO 145 KLOP=1,NDATA
      PRINT*,XX(1,KLOP),XX(2,KLOP),XX(3,KLOP),Y(1,KLOP),Y(2,KLOP)
  145 CONTINUE
      WRITE(6,151)
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PROGRAM RAZZ10     73/730  OPT=2                                  FTN 4.8+587        85/07/2
      151 FORMAT("1","START OF CALCULATIONS BASED ON A WIDE RANGE OF VALUES",
     1" OF V/M ,TAKEN IN INCREASING ORDER"//)
          CALL MVEST(DEL,NFIG,NDATA,RLAM,FACT,RLMAX,RLMIN,MAXITR,NI
  290     1,NO,NPAR,BETA,Y,XX,PN,A,A1,P)
          C1P=CC1P/BETA(1)
          CC1IN=C1INN/BETA(1)
          CNON1F=CFNON1/BETA(1)
          WRITE(6,119)
          WRITE(6,120)
  295     WRITE(6,127) CC1IN, CC2IN
      127 FORMAT(" INITIAL CONCENTRATION OF COMPOUND # 1 = ",E14.6,
     $        "MILLIMOLE / L"//
     $        " INITIAL CONCENTRATION OF COMPOUND # 2 = ",E14.6,
     &        "MILLIMOLE / L"//)
  300     WRITE(6,133)
      133 FORMAT(" ",6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",
     1       " ",13X,"V/M",14X,"NUN"//
     2       " ",3X,"M-MOLE/L",11X,"M-MOLE/L",9X,"M-MOLE/G",9X,
     3       "M-MOLE/G",9X,"LITERS/G"/)
  305     SUM=0.0
          DO 157 J=1,NDATA
          Q1EXP(J)=Q1EXP(J)/BETA(1)
          C1IN(J)=C1IN(J)/BETA(1)
          C1EXP(J)=C1EXP(J)/BETA(1)
  310     SUM=SUM+(A(1,J)**2)+(A(2,J)**2)
          WRITE(6,140) C1EXP(J),C2EXP(J),Q1EXP(J),Q2EXP(J),VMEXP(J),NUN(J)
          CC1=C1EXP(J)
          QC1=Q1EXP(J)
  315     CALL PLOTPT(CC1,QC1,10)
      157 CONTINUE
          WRITE(6,156) SUM
      156 FORMAT("1","///"," ","SUM OF SQUARES OF THE CONCENTRATIONS = ",E16.8)
  320     WRITE(6,5000)
          IF(NPAR.EQ.1) GO TO 158
          FAC1=1./(1.+ABS(BETA(3)))
          FAC2=1./(1.+ABS(BETA(2)))
      158 CONTINUE
          MM1=BETA(1)
  325     FRO=BETA(1)**(PORE(3)-1.)
          K1=PORE(1)*FRO
          K1P=PORE(5)*(BETA(1)**(PORE(7)-1.))
          PAR(8)=C1INN/MM1
          PAR(8)=(C1INN-CFNON1)/MM1
  330     PAR(9)=CC2IN
          PAR(6)=VMEXP(1)
          PAR(1)=(1.-FAC1)*K1
          PAR(2)=(1.-FAC2)*K2
          PAR(18)=FAC1*K1
  335     PAR(19)=FAC2*K2
          PAR(3)=M1
          PAR(4)=M2
          PAR(10)=(1.-FAC1)*K1P
          PAR(11)=(1.-FAC2)*K2P
  340     PAR(12)=FAC1*K1P
          PAR(13)=FAC2*K2P
          PAR(14)=(CC1P-CFNON1)/MM1
          PAR(15)=C2P


PROGRAM RAZZ10     73/730  OPT=2                                  FTN 4.8+587        85/07/2
          PAR(16)=M1P
          PAR(17)=M2P
  345     PRINT*,"PAR( 1 TO 7)= ",(PAR(II),II=1,7)
          PRINT*,"PAR(8 TO 14)= ",(PAR(II),II=8,14)
          PRINT*,"PAR(15)=",PAR(15),," PAR(16)=",PAR(16),," PAR(17)=",PAR(17)
          WRITE(6,151)
          JC1=1
  350     JC2=1
          JVM=1
          DO 1175 J=1,180
          IF(J.LE.5) PAR(5)=0.000010+(J-1)*0.0005
          IF(J.GT.5.AND.J.LE.12) PAR(5)=PAR(5)+0.001
  355     IF(J.GT.12.AND.J.LE.39) PAR(5)=PAR(5)+0.0025
          IF(J.GT.39.AND.J.LE.60) PAR(5)=PAR(5)+0.005
          IF(J.GT.60.AND.J.LE.80) PAR(5)=PAR(5)+0.01
          IF(J.GT.80) PAR(5)=PAR(5)+0.05
  360     PAR(7)=0.5/PAR(5)
          IF(J.GT.1) GO TO 1178
          CC1=0.99*CC1IN
          QC1=0.5*(K1*CC1**M1)
          X(1)=CC1IN-(QC1/PAR(6))
  365     QC2=0.5*(K2*(0.99*CC2IN)**M2)
          X(2)=CC2IN-(QC2/PAR(6))
          PRINT*,"PAR(1 TO 7) = ",(PAR(ILL),ILL=1,7)
          PRINT*,"PAR(8 TO 13) = ",(PAR(ILL),ILL=8,13)
     1170 CONTINUE
  370     WRITE(6,1172) (X(K),K=1,2),PAR(6)
     1172 FORMAT(" ","INITIAL X( K) = ",3(E12.5,1X))
          CALL ZSPONI(FCN,NSIG,N,ITMAX,PAR,X,FNORM,NK,IER)
```

```
      VML(J)=PAR(6)
      PRINT*,"J=",J," IER = ",IER," FNORM=",FNORM," X(1)=",X(1),
     1" X(2)=",X(2)," VML(J)=",VML(J)
375   QL1(J)=(PAR(8)-X(1))*VML(J)
      QL2(J)=(CC2IN-X(2))*VML(J)
      WRITE(6,57) X(1),QL1(J),X(2),QL2(J)
      CL1(J)=X(1)+CNONIF
      CL2(J)=X(2)
380   IF(J.EQ.1) GO TO 7000
      IF(J.NE.25) GO TO 6750
      PRINT*,"JC1=",JC1,"JC2=",JC2," JVM=",JVM
      PRINT*,"C1EXP(JC1)=",C1EXP(JC1),"  CL1(J)=",CL1(J),"  CL1(J-1)="
     1,CL1(J-1),"  JC1=",JC1
385   PRINT*,"C2EXP(JC2)=",C2EXP(JC2),"  CL2(J)=",CL2(J)
     1,"  CL2(J-1)=",CL2(J-1),"  JC2=",JC2
      PRINT*,"VMEXP(JVM)=",VMEXP(JVM),"  VML(J)=",VML(J)
     1,"  VML(J-1)=",VML(J-1),"  JVM=",JVM
      PRINT*,"X(  )=",(X(KOO),KOO=1,2)
390   6750 CONTINUE
      IF(JC1.GT.NP) GO TO 6800
      IF(CL1(J).LT.C1EXP(JC1).AND.CL1(J-1).GE.C1EXP(JC1)) GO TO 6900
      PRINT*,"AFTER 6750, JC1=",JC1,"  JC2=",JC2,"  JVM=",JVM
      6800 CONTINUE
395   IF(JC2.GT.NP) GO TO 6810
      IF(CL2(J).LT.C2EXP(JC2).AND.CL2(J-1).GE.C2EXP(JC2)) GO TO 6950
      PRINT*,"AFTER 6800, JC1=",JC1,"  JC2=",JC2,"  JVM=",JVM
      6810 CONTINUE
      IF(JVM.GT.NP) GO TO 7000
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      PROGRAM RAZZ10     73/730  OPT=2                    FTN 4.8+587      85/07/29

400   IF(VML(J).LT.VMEXP(JVM).AND.VML(J-1).GE.VMEXP(JVM)) GO TO 6975
      PRINT*,"AFTER 6810, JC1=",JC1,"  JC2=",JC2,"  JVM=",JVM
      GO TO 7000
      6900 CONTINUE
      6905 CONTINUE
405   XC1(JC1,2)=X(2)
      XC1(JC1,1)=VML(J)
      PRINT*,"J=",J," JC1=",JC1," XC1(JC1,1)=",XC1(JC1,1),XC1(JC1,2)
      JC1=JC1+1
      IF(JC1.GT.NP) GO TO 6800
410   IF(C1EXP(JC1).GT.C1EXP(JC1-1)) GO TO 6900
      GO TO 6750
      6950 CONTINUE
      PRINT*,"J=",J," JC2=",JC2
      6955 CONTINUE
415   XC2(JC2,1)=X(1)
      XC2(JC2,2)=VML(J)
      PRINT*,"J=",J," JC2=",JC2," XC2(JC2,2)=",XC2(JC2,2)
      JC2=JC2+1
      IF(JC2.GT.NP) GO TO 6810
420   IF(C2EXP(JC2).GT.C2EXP(JC2-1)) GO TO 6950
      GO TO 6800
      6975 CONTINUE
      PRINT*,"J=",J," JVM=",JVM
      DO 6980 KITE=1,2
425   XVM(JVM,KITE)=X(KITE)
      6980 CONTINUE
      PRINT*,"J=",J," JVM=",JVM," XVM(JVM,1)=",XVM(JVM,1)
      JVM=JVM+1
      IF(JVM.GT.NP) GO TO 7000
430   IF(VMEXP(JVM).GT.VMEXP(JVM-1)) GO TO 6975
      GO TO 6810
      7000 CONTINUE
      PRINT*,"MENT BY 7000"
      1175 CONTINUE
435   NPOT=J
      IF(NPOT.GT.100) NPOT=100
      PRINT*,"JC1=",JC1,"  JC2=",JC2,"   JVM=",JVM," NPOT=",NPOT
      NPP=JC1
      IF(JC2.LT.NPP) NPP=JC2
440   IF(JVM.LT.NPP) NPP=JVM
      NPP=NPP-1
      PRINT*,"NPP=",NPP,"  JC1=",JC1,"  JC2=",JC2,"  JVM=",JVM
      PRINT*,"  MATRIX XC1="
      DO 7100 KOOL=1,NPP
445   PRINT*,(XC1(KOOL,KIK),KIK=1,2)
      7100 CONTINUE
C
      WRITE(6,100)
      WRITE(6,104)
450   WRITE(6,120)TEST,COMP1,COMP2
      WRITE(6,125)  CC1IN,CC2IN
      WRITE(6,128)
      128  FORMAT(1H1,"///"  ",73X,"GIVEN"//)
      WRITE(6,131)
455   131 FORMAT(1H ,"  ",6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",
     1       "  ",13X,"V/M"//)
```

```
                CALL ZSPOW(FCN2,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
      C
            QQ1(J)=(PAR(8)-X(1))*X(2)
      550   QQQ2(J)=(PAR(9)-C2EXP(J))*X(2)
            PRINT*,"IER=",IER," X(1)=",X(1)," X(2)=",X(2)
            WRITE(6,31)
            WRITE(6,57) X(1),QQ1(J),C2EXP(J),QQQ2(J),X(2)
      555      CFF1(J)=X(1)*CNONIF
               CFF2(J)=C2EXP(J)
               VMF(J)=X(2)
               SUMSQ=SUMSQ+(Q2EXP(J)-QQQ2(J))**2
            SUMSQM=SUMSQP+((Q2EXP(J)-QQQ2(J))*MW2)**2
      560      REDSUM=REDSUM+(1.-QQQ2(J)/Q2EXP(J))**2
       5000 CONTINUE
            WRITE(6,100)
            WRITE(6,107)
        107 FORMAT(" ",' IT USES THE TWO MASS BALANCES AND REQUIRES THE "
           1," INITIAL LIQUID PHASE CONCENTRATIONS"/" ",' OF BOTH COMPONENTS"
      565  2," AND EQUILIBRIUM LIQUID PHASE CONCENTRATION OF COMPONENT NO. 2",
           3//)
            WRITE(6,120) TEST,COMP1,COMP2
            WRITE(6,125) CC1IN, CC2IN
            WRITE(6,1128)
      570 1128 FORMAT(" ",17X,"EXPERIMENTAL",41X,"EXPERIMENTAL",5X,"EXPERIMENTAL",
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PROGRAM RAZZ10     73/730  OPT=2                    FTN 4.8+587        85/87/29

           118X,"EXPERIMENTAL"/)
            WRITE(6,132)
      C
            DO 1150 I=1,NPP
      575      WRITE(6,200) CFF1(I),CFF2(I),QQ1(I),QQQ2(I),Q1EXP(I)
           1,Q2EXP(I),VMF(I),VMEXP(I)
       1150 CONTINUE
            WRITE(6,2151) NPP,SUMSQ,REDSUM
       2151 FORMAT(1H1,"////"," ",5X,"SUMS OF SQUARES OF Q1 AND Q2 IN M-MOLE/G"
      580  1," BASED ON ",I3," POINTS"//" ",
           1"SUM OF SQUARES =  ",E14.6//" ","REDUCED SUM OF THE REDUCED "
           2,"SQUARES = "E14.6///)
            WRITE(6,2149) NPP,SUMSQM
       2149 FORMAT(1H1,"////"," ",5X,"SUMS OF SQUARES OF Q1 AND Q2 IN M-GRAM/G"
      585  1," BASED ON ",I3," POINTS"//" ",
           1"SUM OF SQUARES = ",E14.6///////)
            WRITE(6,2152)
       2152 FORMAT("1"," ","START OF CALCULATIONS BASED ON THE EXPERIMENTAL"
           1," VALUES OF V/M")
      590   CSUMSQM=0.0
            CSUMSQ=0.0
            CREDSUM=0.0
            DO 6000 J=1,NPP
            PAR(8)=C1IN(J)-CNONIF
      595   PAR(9)=C2IN(J)
            PAR(5)=MEXP(J)
            PAR(6)=VEXP(J)/MEXP(J)
            DO 6526 KITE=1,2
            X(KITE)=XVM(J,KITE)
      600 6526 CONTINUE
            KK=1
               WRITE(6,30)KK,X(KK)
               DO 6532 KK=2,N
                  WRITE(6,29)KK,X(KK)
      605 6532    CONTINUE
               PRINT*,"   PAR = ",(PAR(KT),KT=1,7)
      C
      C        CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
      C
      610      PRINT*,"IER=",IER," X(1)=",X(1)," X(2)=",X(2)
               WRITE(6,31)
            VMF(J)=PAR(6)
            QQ1(J)=(PAR(8)-X(1))*VMF(J)
            QQQ2(J)=(PAR(9)-X(2))*VMF(J)
      615   WRITE(6,57) X(1),QQ1(J),X(2),QQQ2(J),VMF(J)
               CFF1(J)=X(1)+CNONIF
               CFF2(J)=X(2)
            CSUMSQ=CSUMSQ+(C1EXP(J)-X(1))**2+(C2EXP(J)-X(2))**2
            CREDSUM=CREDSUP+(1.-X(1)/C1EXP(J))**2+(1.-X(2)/C2EXP(J))**2
      620   CSUMSQM=CSUMSQP+((C1EXP(J)-X(1))*MW1)**2+
           1          ((C2EXP(J)-X(2))*MW2)**2
       6000 CONTINUE
            WRITE(6,100)
            WRITE(6,104)
      625  104 FORMAT(" ",' IT USES THE TWO MASS BALANCES AND REQUIRES THE "
           1," INITIAL LIQUID PHASE CONCENTRATIONS"/" ",' OF BOTH COMPONENTS"
           2," AND THE ACTIVATED CARBON CONCENTRATION"///)
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      PROGRAM RAZZ10     73/730  OPT=2                          FTN 4.8+587        85/07/29

     1       " ",3X,"M-MOLE/L",11X,"M-MOLE/L",9X,"M-MOLE/G",9X,
     1       "M-MOLE/G",9X,"LITERS/G")
  132 FORMAT(" ",6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",
     1       " ",13X,"Q-1",14X,"Q-2",13X,"V/M",12X,"V/M"//
     1       " ",3X,"M-MOLE/L",11X,"M-MOLE/L",9X,"M-MOLE/G",9X,
     1       "M-MOLE/G",9X,"M-MOLE/G",9X,"M-MOLE/G",9X,"LITERS/G",
     1       7X,"LITERS/G"/)
      DO 2150 I=1,NPOT
      WRITE(6,200) CL1(I),CL2(I),QL1(I),QL2(I),VML(I)
      CC1=CL1(I)
      QL1=QL1(I)
      CC1A=CC1-CNON1F
      QPURE1=K1*CC1A**N1
      IF(CC1A.GT.PAR(14)) QPURE1=K1P*CC1A**N1P
      CALL PLOTPT(CC1,QLL1,9)
      CALL PLOTPT(CC1,QPURE1,4)
 2150 CONTINUE
      WRITE(6,31)
   25 FORMAT("1","START OF CALCULATIONS BASED ON THE EXPERIMENTAL "
     1,"VALUES OF C1")

      SUMSQ=0.0
      REDSUM=0.0
      DO 1500 J=1,APP
      PAR(8)=C1IN(J)-CNON1F
      PAR(9)=C2IN(J)
      PAR(5)=C1EXP(J)-CNON1F
      DO 26 KITE=1,2
      X(KITE)=XC1(J,KITE)
   26 CONTINUE
      KK=2
      WRITE(6,30)KK,X(KK)
      DO 32 KK=2,N
      WRITE(6,29)KK,X(KK)
   32 CONTINUE
      PRINT*,"    PAR = ",(PAR(KT),KT=1,7)
C
      CALL ZSPOW(FCN1,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
C
      PRINT*,"IER=",IER," X(1)=",X(1)," X(2)=",X(2)
      WRITE(6,31)
      QQ1(J)=(PAR(8)-PAR(5))*X(1)
      QQ2(J)=(PAR(9)-X(2))*X(1)
   70 CONTINUE
      CF1(J)=C1EXP(J)
      CF2(J)=X(2)
      VMF(J)=X(1)
      SUMSQ=SUMSQ+(Q1EXP(J)-QQ1(J))**2
      REDSUM=REDSUM+(1.-QQ1(J)/Q1EXP(J))**2
 1500 CONTINUE
      PRINT*," SUM OF SQUARES =",SUMSQ
      PRINT*," REDUCED SUM = ",REDSUM
      SUMSQM=SUMSQ*(FM1**2)
C
      WRITE(6,100)
  100 FORMAT(" ","  IT USES THE TWO MASS BALANCES AND REQUIRES THE "
     1"INITIAL LIQUID PHASE CONCENTRATIONS"/" ","  OF BOTH COMPONENTS"

     2," AND EQUILIBRIUM LIQUID PHASE CONCENTRATION OF COMPONENT NO. 1",
     3"/)
      WRITE(6,120) TEST,COMP1,COMP2
      WRITE(6,125) CC1IN, CC2IN
      WRITE(6,129)
  129 FORMAT(" ",3X,"EXPERIMENTAL",5X,"EXPERIMENTAL",5X,"EXPERIMENTAL",
     1213X,"EXPERIMENTAL"/)
      WRITE(6,132)
C
      DO 3150 I=1,APP
      WRITE(6,200) CF1(I),CF2(I),QQ1(I),QQ2(I),Q1EXP(I)
     1,Q2EXP(I),VMF(I),VMEXP(I)
      CC1=CF1(I)
      QC1=QQ1(I)
      CALL PLOTPT(CC1,QC1,2)
 3150 CONTINUE
      WRITE(6,3151)
 3151 FORMAT("1","START OF CALCULATIONS BASED ON THE EXPERIMENTAL "
     1,"VALUES OF C2"///)
      DO 5000 J=1,APP
      PAR(8)=C1IN(J)-CNON1F
      PAR(9)=C2IN(J)
      PAR(6)=C2EXP(J)
      DO 526 KITE=1,2
      X(KITE)=XC2(J,KITE)
  526 CONTINUE
      KK=1
      WRITE(6,30)KK,X(KK)
      DO 532 KK=2,N
      WRITE(6,29)KK,X(KK)
  532 CONTINUE
      PRINT*,"    PAR = ",(PAR(KT),KT=1,7)
C
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PROGRAM RAZZLO      73/730  OPT=2                          FTN 4.8+587        85/07/29

                WRITE(6,120) TEST,COMP1,COMP2
                WRITE(6,125) CC1IN, CC2IN
                WRITE(6,6128)
630          6128 FORMAT(" ",70X,"EXPERIMENTAL",5X,"EXPERIMENTAL",
               1 18X,"EXPERIMENTAL"/)
                WRITE(6,132)
             C
635             DO 6150 I=1,NPP
                  WRITE(6,200) CF1(I),CFF2(I),QQ1(I),QQQ2(I),Q1EXP(I)
               1,Q2EXP(I),VMF(I),VMEXP(I)
             6150 CONTINUE
                WRITE(6,152) NPP,CSUMSQ,CREDSUM
640          152 FORMAT(" "/////" ",5X,"SUMS OF SQUARES OF C1 AND C2 IN M-MOLES/L"
               1," BASED ON ",I3," POINTS"/" "
               1"SUM OF SQUARES = ",E14.6//" ","REDUCED SUM OF THE REDUCED "
               2,"SQUARES = "E14.6///)
                WRITE(6,149) NPP,CSUMSQM
645          149 FORMAT(" "/////" ",5X,"SUMS OF SQUARES OF C1 AND C2 IN M-GRAMS/L"
               1," BASED ON ",I3," POINTS"/" ",
               1"SUM OF SQUARE = ",E14.6///////)
             C
                WRITE(6,1005)
650          1005 FORMAT(" "////" THE FIRST GRAPH PRESENTS THE ISOTHERMS OF",
                    2       = COMPONENT # 1 AND THE SECOND GRAPH PRESENTS",
                    3       = THE ISOTHERMS OF COMPONENT # 2"///)
             C
                WRITE(6,1010)
655          1010 FORMAT(" LEGEND OF GRAPH BELOW"/,
                    1       = ----------------------"/,
                    2       = + = PREDICTED MULTICOMPONENT ISOTHERM"/,
                    3       = O = OBSERVED MULTICOMPONENT ISOTHERM"/,
                    4       = * = SINGLE COMPONENT ISOTHERM")
660          C
             C
               200 FORMAT(" ",6(E14.6,3X),E14.6,1X,E14.6)
                CALL OUTPLT
             C
665             DO 220 I=1,NP
                   CC2=C2EXP(I)
                   QCC2=Q2EXP(I)
                   CALL PLOTPT(CC2,QCC2,18)
               220 CONTINUE
678             DO 2220 I=1,180
                CC2=CL2(I)
                QC2=QL2(I)
                QPURE2=K2*CC2**N2
                CALL PLOTPT(CC2,QC2,9)
675             CALL PLOTPT(CC2,QPURE2,4)
              2220 CONTINUE
                CALL OUTPLT
             C
680             WRITE(6,100)
                WRITE(6,120) TEST, COMP1, COMP2
                WRITE(6,225) C1INM, C2INM
               225 FORMAT(" INITIAL CONCENTRATION OF COMPUNO # 1 = ",E14.6,
                    2       = MILLIGRAM / L"//
                    3       INITIAL CONCENTRATION OF COMPOUND # 2 = ",E14.6,
```

```
SUBROUTINE FCN2      73/730  OPT=2                          FTN 4.8+587        85/07/2

1               SUBROUTINE FCN2(G,F,N,PAR)
                INTEGER N
                REAL G(N),F(N),PAR(31)
                IF(G(1).GT.0.0.OR.PAR(6).LT.0.0) GO TO 5
5               PRINT*,"          G(1)=",G(1),"  PAR(6)=",PAR(6)
                CONTINUE
                IF(G(1).GT.PAR(14)) GO TO 20
                IF(PAR(6).GT.PAR(15)) GO TO 10
10              F(1)=(PAR(8)-G(1))*G(2)-((PAR(18)*(G(1)/(G(1)+PAR(6)))**PAR(3))
               1*(G(1)**PAR(3)))      -(PAR(1)*G(1)**PAR(3))
                F(2)=((PAR(9)-PAR(6))*G(2))-((PAR(19)*(PAR(6)/(G(1)+PAR(6)))
               1**PAR(4))*(PAR(6)**PAR(4)))      -(PAR(2)*PAR(6)**PAR(4))
                GO TO 40
15           10 CONTINUE
                F(1)=(PAR(8)-G(1))*G(2)-((PAR(18)*(G(1)/(G(1)+PAR(6)))**PAR(3))
               1*(G(1)**PAR(3)))      -(PAR(1)*G(1)**PAR(3))
                F(2)=((PAR(9)-PAR(6))*G(2))-((PAR(13)*(PAR(6)/(G(1)+PAR(6)))
               1**PAR(17))*(PAR(6)**PAR(17)))      -(PAR(11)*PAR(6)**PAR(17))
                GO TO 40
20           20 IF(PAR(6).GT.PAR(15)) GO TO 30
                F(1)=(PAR(8)-G(1))*G(2)-((PAR(12)*(G(1)/(G(1)+PAR(6)))**PAR(16))
               1*(G(1)**PAR(16)))      -(PAR(1)*G(1)**PAR(16))
                F(2)=((PAR(9)-PAR(6))*G(2))-((PAR(19)*(PAR(6)/(G(1)+PAR(6)))
               1**PAR(4))*(PAR(6)**PAR(4)))      -(PAR(2)*PAR(6)**PAR(4))
25              GO TO 40
             30 CONTINUE
                F(1)=(PAR(8)-G(1))*G(2)-((PAR(12)*(G(1)/(G(1)+PAR(6)))**PAR(16))
               1*(G(1)**PAR(16)))      -(PAR(1)*G(1)**PAR(16))
                F(2)=((PAR(9)-PAR(6))*G(2))-((PAR(13)*(PAR(6)/(G(1)+PAR(6)))
               1**PAR(17))*(PAR(6)**PAR(17)))      -(PAR(11)*PAR(6)**PAR(17))
             40 CONTINUE
                RETURN
                END
```

```
      PROGRAM RAZZ10     73/730  OPT=2                                FTN 4.8+587        85/07/25
     4        " MILLIGRAM / L"////)
       WRITE(6,230)
  230 FORMAT(" ",6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",
     1   13X,"V/M"/)
     1" ",3X,"MILLIG/L",11X,"MILLIG/L",9X,"MILLIG/G",9X,"MILLIG/G",
     10X,"LITERS/G"//)
C
       DO 250 I=1,NP
          CC1=C1EXP(I)=C1EXP(I)*MW1
          CC2=C2EXP(I)=C2EXP(I)*MW2
          Q1EXP(I)=Q1EXP(I)*MW1
          Q2EXP(I)=Q2EXP(I)*MW2
          QC1=Q1EXP(I)
          CALL PLOTPT(CC1,QC1,2)
          WRITE(6,200) CC1,CC2,QC1,Q2EXP(I),VMEXP(I)
  250 CONTINUE
       WRITE(6,100)
       WRITE(6,120)  TEST, COMP1, COMP2
       WRITE(6,125) C1INM, C2INM
       WRITE(6,120)
       WRITE(6,231)
  231 FORMAT(" ",6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",13X,"V/M"////
     1" ",3X,"MILLIG/L",11X,"MILLIG/L",9X,"MILLIG/G",9X,"MILLIG/G"
     2,11X,"LITERS/G"//)
       DO 2250 I=1,100
       CC1=CL1(I)=CL1(I)*MW1
       QC1=QL1(I)=QL1(I)*MW1
       CC1A=CC1-CFNCN1
       QCC1=KK1*CC1A**N1
       IF(CC1.GT.CC1P) QCC1=KK1P*CC1A**N1P
       QL2(I)=QL2(I)*MW2
       CL2(I)=CL2(I)*MW2
       CALL PLOTPT(CC1,QC1,9)
       CALL PLOTPT(CC1,QCC1,4)
       WRITE(6,200)CC1,CL2(I),QC1,QL2(I),VML(I)
 2250 CONTINUE
C
       CALL OUTPLT
C
       DO 260 I=1,NP
          CC2=C2EXP(I)
          QCC2=Q2EXP(I)
          CALL PLOTPT(CC2,QCC2,10)
  260  CONTINUE
       DO 2260 I=1,100
       CC2=CL2(I)
       QC2=QL2(I)
       QCC2=KK2*CC2**N2
       CALL PLOTPT(CC2,QC2,9)
       CALL PLOTPT(CC2,QCC2,4)
 2260 CONTINUE
C
       CALL OUTPLT
   29     FORMAT(" ",-                    X(",I2,") = ",E14.6)
   30    FORMAT("0",-INITIAL GUESSES OF X(",I2,") = ",E14.6)
   31    FORMAT(" ",11X,8X,"C1",7X,"Q1",
     1   9X,"C2",11X,"Q2",9X,"V/M")
```

```
      PROGRAM RAZZ10     73/730  OPT=2                                FTN 4.8+587        85/07/25
  57    FORMAT(" ",8X,10(E11.4,1X))
  100 FORMAT("1",3X,"PREDICTIVE PRELIMINARY ISOTHERM CALCULATIONS BASED
     1 ON THE RAZZAK-HI COMPETITIVE ADSORPTION MODEL"//)
       PRINT*," KK1P=",KK1P," N1P=",N1P," CFNCN1=",CFNCN1
       TH(1)=KK1
       TH(2)=N1
       TH(3)=999.
       NPROB=2
       NOB=NP
       TH(4)=KK1P
       TH(5)=N1P
       CNON=CFNCN1
       CDIV=CC1P
       CALL ISOPLOT(NPROB,TH,C1EXP,Q1EXP,CL1,QL1,NO3,NP,NUM,
     1CNON,CDIV,NPCT)
       TH(1)=KK2/((1000.0)**N2)
       TH(2)=N2
       TH(3)=999.
       DO 3000 I=1,NP
 3000 C2EXP(I)=C2EXP(I)*1000.0
       DO 3010 I=1,100
 3010 CL2(I)=CL2(I)*1000.0
       NPROB=2
       TH(4)=KK2P/((1000.0**N2P)
       TH(5)=N2P
       CNON=0.00
       CDIV=CC2P
       NOB=NP
       CALL ISOPLOT(NPROB,TH,C2EXP,Q2EXP,CL2,QL2,NO3,NP,NUM,
     1CNON,CDIV,NPCT)
       CALL PLOT(0.0,0.0,999)
       STOP
       END
```

```
      SUBROUTINE FCN(G,F,N,PAR)
      INTEGER N
      REAL G(N),F(N),PAR(31)
      IF(G(1).GT.0.0.OR.G(2).LT.0.0) GO TO 5
      PRINT*,'                G(1)=',G(1),'  G(2)=',G(2)
    5 CONTINUE
      IF(G(1).GT.PAR(14)) GO TO 20
      IF(G(2).GT.PAR(15)) GO TO 10
      F(1)=(PAR(8)-G(1))*PAR(6)-((PAR(18)*(G(1)/(G(1)+G(2)))**PAR(3))
     1*(G(1)**PAR(3)))      -(PAR(1)*G(1)**PAR(3))
      F(2)=((PAR(9)-G(2))*PAR(6)-((PAR(19)*(G(2)/(G(1)+G(2)))**PAR(4))
     1*(G(2)**PAR(4)))      -(PAR(2)*G(2)**PAR(4))
      GO TO 40
   10 CONTINUE
      F(1)=(PAR(8)-G(1))*PAR(6)-((PAR(18)*(G(1)/(G(1)+G(2)))**PAR(3))
     1*(G(1)**PAR(3)))      -(PAR(1)*G(1)**PAR(3))
      F(2)=((PAR(9)-G(2))*PAR(6)-((PAR(13)*(G(2)/(G(1)+G(2)))**PAR(17))
     1*(G(2)**PAR(17)))     -(PAR(11)*G(2)**PAR(17))
      GO TO 40
   20 IF(G(2).GT.PAR(15)) GO TO 30
      F(1)=(PAR(8)-G(1))*PAR(6)-((PAR(12)*(G(1)/(G(1)+G(2)))**PAR(16))
     1*(G(1)**PAR(16)))     -(PAR(10)*G(1)**PAR(16))
      F(2)=((PAR(9)-G(2))*PAR(6)-((PAR(19)*(G(2)/(G(1)+G(2)))**PAR(4))
     1*(G(2)**PAR(4)))      -(PAR(2)*G(2)**PAR(4))
      GO TO 40
   30 CONTINUE
      F(1)=(PAR(8)-G(1))*PAR(6)-((PAR(12)*(G(1)/(G(1)+G(2)))**PAR(16))
     1*(G(1)**PAR(16)))     -(PAR(10)*G(1)**PAR(16))
      F(2)=((PAR(9)-G(2))*PAR(6)-((PAR(13)*(G(2)/(G(1)+G(2)))**PAR(17))
     1*(G(2)**PAR(17)))     -(PAR(11)*G(2)**PAR(17))
   40 CONTINUE
      RETURN
      END
```

SUBROUTINE FCN1 73/738 OPT=2 FTN 4.8+587 85/07/2

```
      SUBROUTINE FCN1(G,F,N,PAR)
      INTEGER N
      REAL G(N),F(N),PAR(31)
      IF(PAR(5).GT.0.0.OR.G(2).LT.0.0) GO TO 5
      PRINT*,'                PAR(5)=',PAR(5),'  G(2)=',G(2)
    5 CONTINUE
      IF(PAR(5).GT.PAR(16)) GO TO 20
      IF(G(2).GT.PAR(15)) GO TO 10
      F(1)=(PAR(8)-PAR(5))*G(1)-((PAR(18)*(PAR(5)/(PAR(5)+G(2)))**
     1PAR(3))*(PAR(5)**PAR(3)))     -(PAR(1)*PAR(5)**PAR(3))
      F(2)=((PAR(9)-G(2))*G(1)-((PAR(19)*(G(2)/(PAR(5)+G(2)))**PAR(4))
     1*(G(2)**PAR(4)))      -(PAR(2)*G(2)**PAR(4))
      GO TO 40
   10 CONTINUE
      F(1)=(PAR(8)-PAR(5))*G(1)-((PAR(18)*(PAR(5)/(PAR(5)+G(2)))
     1**PAR(3))*(PAR(5)**PAR(3)))     -(PAR(1)*PAR(5)**PAR(3))
      F(2)=((PAR(9)-G(2))*G(1)-((PAR(13)*(G(2)/(PAR(5)+G(2)))**PAR(17))
     1*(G(2)**PAR(17)))     -(PAR(11)*G(2)**PAR(17))
      GO TO 40
   20 IF(G(2).GT.PAR(15)) GO TO 30
      F(1)=(PAR(8)-PAR(5))*G(1)-((PAR(12)*(PAR(5)/(PAR(5)+G(2)))
     1**PAR(16))*(PAR(5)**PAR(16)))     -(PAR(10)*PAR(5)**PAR(16))
      F(2)=((PAR(9)-G(2))*G(1)-((PAR(19)*(G(2)/(PAR(5)+G(2)))**PAR(4))
     1*(G(2)**PAR(4)))      -(PAR(2)*G(2)**PAR(4))
      GO TO 40
   30 CONTINUE
      F(1)=(PAR(8)-PAR(5))*G(1)-((PAR(12)*(PAR(5)/(PAR(5)+G(2)))
     1**PAR(16))*(PAR(5)**PAR(16)))     -(PAR(10)*PAR(5)**PAR(16))
      F(2)=((PAR(9)-G(2))*G(1)-((PAR(13)*(G(2)/(G(1)+G(2)))**PAR(17))
     1*(G(2)**PAR(17)))     -(PAR(11)*G(2)**PAR(17))
   40 CONTINUE
      RETURN
      END
```

SUBROUTINE FCN2 73/738 OPT=2 FTN 4.8+587 85/07/2

```
      SUBROUTINE FCN2(G,F,N,PAR)
      INTEGER N
      REAL G(N),F(N),PAR(31)
      IF(G(1).GT.0.0.OR.PAR(6).LT.0.0) GO TO 5
      PRINT*,'                G(1)=',G(1),'  PAR(6)=',PAR(6)
    5 CONTINUE
      IF(G(1).GT.PAR(14)) GO TO 20
      IF(PAR(6).GT.PAR(15)) GO TO 10
      F(1)=(PAR(8)-G(1))*G(2)-((PAR(18)*(G(1)/(G(1)+PAR(6)))**PAR(3))
     1*(G(1)**PAR(3)))      -(PAR(1)*G(1)**PAR(3))
      F(2)=((PAR(9)-PAR(6))*G(2)-((PAR(19)*(PAR(6)/(G(1)+PAR(6)))
     1**PAR(4))*(PAR(6)**PAR(4)))     -(PAR(2)*PAR(6)**PAR(4))
      GO TO 40
   10 CONTINUE
      F(1)=(PAR(8)-G(1))*G(2)-((PAR(18)*(G(1)/(G(1)+PAR(6)))**PAR(3))
     1*(G(1)**PAR(3)))      -(PAR(1)*G(1)**PAR(3))
      F(2)=((PAR(9)-PAR(6))*G(2)-((PAR(13)*(PAR(6)/(G(1)+PAR(6)))
     1**PAR(17))*(PAR(6)**PAR(17)))     -(PAR(11)**PAR(6)**PAR(17))
      GO TO 40
   20 IF(PAR(6).GT.PAR(15)) GO TO 30
      F(1)=(PAR(8)-G(1))*G(2)-((PAR(12)*(G(1)/(G(1)+PAR(6)))**PAR(16))
     1*(G(1)**PAR(16)))     -(PAR(10)*G(1)**PAR(16))
      F(2)=((PAR(9)-PAR(6))*G(2)-((PAR(19)*(PAR(6)/(G(1)+PAR(6)))
     1**PAR(4))*(PAR(6)**PAR(4)))     -(PAR(2)*PAR(6)**PAR(4))
      GO TO 40
   30 CONTINUE
      F(1)=(PAR(8)-G(1))*G(2)-((PAR(12)*(G(1)/(G(1)+PAR(6)))**PAR(16))
     1*(G(1)**PAR(16)))     -(PAR(10)*G(1)**PAR(16))
      F(2)=((PAR(9)-PAR(6))*G(2)-((PAR(13)*(PAR(6)/(G(1)+PAR(6)))
     1**PAR(17))*(PAR(6)**PAR(17)))     -(PAR(11)*PAR(6)**PAR(17))
   40 CONTINUE
      RETURN
      END
```

```
SUBROUTINE MODEL      73/730  OPT=2                    FTN 4.8+587        85/07/29

      1               SUBROUTINE MODEL(Y,XX,BETA,NPAR,A,NDATA,NI,NO)
                      DIMENSION BETA(3),Y(NO,NDATA),XX(NI,NDATA),A(NO,NDATA)
                      DIMENSION WK(500),PAR(31),F(3),G(2)
                      REAL K1,K1P,FNORM
      5               COMMON /POW/ NSIG,N,ITMAX,PORE(31),FAC1,FAC2,Z1
                      EXTERNAL FCN
                      IF(NPAR.EQ.1) GO TO 20
                      FAC1=1./(1.+ABS(BETA(3)))
                      FAC2=1./(1.+ABS(BETA(2)))
     10           20  CONTINUE
                      FRO=BETA(1)**(PORE(3)-1.)
                      K1=PORE(1)*FRO
                      K1P=PORE(5)*(BETA(1)**(PORE(7)-1.))
                      PAR(1)=(1.-FAC1)*K1
     15               PAR(2)=(1.-FAC2)*PORE(2)
                      PAR(18)=FAC1*K1
                      PAR(19)=FAC2*PORE(2)
                      PAR(3)=PORE(3)
                      PAR(4)=PORE(4)
     20               PAR(10)=(1.-FAC1)*K1P
                      PAR(11)=(1.-FAC2)*PORE(6)
                      PAR(12)=FAC1*K1P
                      PAR(13)=FAC2*PORE(6)
                      PAR(14)=PORE(9)/BETA(1)
     25               PAR(15)=PORE(10)
                      PAR(16)=PORE(7)
                      PAR(17)=PORE(8)
                      DO 100 I=1,NDATA
                       G(1)=Y(1,I)/BETA(1)
     30                G(2)=Y(2,I)
                       PAR(8)=XX(1,I)/BETA(1)
                      PAR(9)=XX(2,I)
                      PAR(6)=XX(3,I)
                      CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,G,FNORM,WK,IER)
     35               IF(IER.NE.0) PRINT*,"IER=",IER," I=",I," FNORM=",FNORM,
                     1" G(1)=",G(1)," G(2)=",G(2)
                      A(1,I)=Y(1,I)-G(1)*BETA(1)
                      A(2,I)=Y(2,I)-G(2)
     100              CONTINUE
     40               RETURN
                      END
```

APPENDIX H2

LISTING OF COMPUTER PROGRAM BASED ON THE MSCAM MODEL FOR BISOLUTE ADSORPTION ISOTHERMS

The program used for the parameter estimation of the MSCAM model was called MSIAS and is listed below. This program is very similar to that of the Razzaghi model (RAZZI0) and the comments about RAZZI0 are also applicable to MSIAS (see the beginning of Appendix H1).

```
PROGRAM MSIAS      73/738  OPT=2                                  FTN 4.8+587      85/07/30
      PROGRAM MSIAS(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      DIMENSION CF1(31),CF2(31),QQ1(31),QQ2(31)
      DIMENSION C1EXP(31),C2EXP(31),VEXP(31),VMEXP(31),VMF(31)
      DIMENSION CL1(100),CL2(100),QL1(100),QL2(100),VML(100)
      DIMENSION CFF2(31),QQQ2(31)
      DIMENSION BETA(9),Y(2,31),XX(3,31),PW(2,31,3),A1(2,31),A(2,31)
     1,P(2,31)
      DIMENSION C1IN(31),C2IN(31)
      DIMENSION PAR(30),X(11),XC1(31,11),XC2(31,11),XVM(31,11)
      DIMENSION TM(5),WK(500)
      REAL MEXP(31)
      REAL K1,KK1,K2,KK2,MW1,MW2,N1,N2
      REAL KK1P,KK2P,K1P,K2P,N1P,N2P
      INTEGER TEST(4),COMP1(4),COMP2(4)
      COMMON /POW/ MSIG,N,ITMAX,PORE(31),FAC1,FAC2,Z1
      COMMON /DATA/ Q1EXP(31),Q2EXP(31),NUN(31)
      EXTERNAL FCN,FCN1,FCN2,MODEL
C*********************************************************************
C
C          M S I A S
C
C*********************************************************************
C*********************************************************************
C
C        PROGRAM THAT REGRESSES THE COMPETITIVE ADSORPTION ISOTHERM    C
C        DATA TO THE MODIFIED IAS COMPETITIVE ISOTHERM MODEL           C
C                                                                      C
C*********************************************************************C
C*********************************************************************
C
C     ASSUMPTIONS
C                  1) THE ADSORPTION ISOTHERM OF BOTH COMPONENTS CAN BE
C                     DESCRIBED BY FREUNDLICH ISOTHERM MODELS
C                  2) ALL THOSE ASSUMPTIONS INHERENT WITH THE
C                     MODIFIED IAS COMPETITIVE ISOTHERM MODEL
C                  3) ALL THOSE ASSUMPTIONS INHERENT WITH USING THE
C                     IMSL ROUTINE "ISPOW" (IT SOLVES SIMULTANEOUS
C                     NON-LINEAR EQUATIONS USING A MODIFIED NEWTON'S
C                     METHOD)
C*********************************************************************
C
C     DEVELOPED BY R.M. NARBAITZ AT MCMASTER UNIV. IN MARCH 1985
C*********************************************************************
C
      NW=2
      READ(5,*) ITMAX,MSIG,NP
      READ(5,20)TEST
   20 FORMAT(4A10)
      READ(5,20) COMP1
      READ(5,20) COMP2
      READ(5,*)C1INM,C2INM
```

```
PROGRAM MSIAS      73/738  OPT=2                                  FTN 4.8+587      85/07/30
      READ(5,*) MW1,MW2,KK1,KK2,N1,N2,CFNON1
      READ(5,*) CC1P,CC2P,KK1P,KK2P,N1P,N2P
      READ(5,*) QM1M,QM2M,BB1,BB2,CLNON1
      READ(5,*)CCQ1P,CCQ2P,QM1MP,QM2MP,BB1P,BB2P
      READ(5,*) NDATA,NO,NI,NPAR
      READ(5,*)(BETA(I),I=1,NPAR)
      READ(5,*) MAXITR,DEL,NFIG
      READ(5,*) RLAM,FACT,RLMAX,RLMIN
      READ(5,*) FAC1,FAC2,Z1
      MW1=BETA(1)

       CC1IN = C1INM / MW1
       CC2IN = C2INM / MW2
      QM1=QM1M/MW1
      B1=BB1*MW1
      K2=KK2*(MW2)**(N2-1.)
      K2P=KK2P*(MW2)**(N2P-1.)
      K1=KK1*(MW1)**(N1-1.)
      K1P=KK1P*(MW1)**(N1P-1.)
      C1P=CC1P/MW1
      C2P=CC2P/MW2
      CQ1P=CCQ1P/MW1
      CQ2P=CCQ2P/MW2
      QM1P=QM1MP/MW1
      QM2P=QM2MP/MW2
      B1P=BB1P*MW1
      B2P=BB2P*MW2
      CNON1F=CFNCN1/MW1
      CNON1L=CLNON1/MW1
      QM2=QM2M/MW2
      B2=BB2*MW2
      PRINT*,"
     ---*,"          -- NP =",NP," = NUMBER OF POINTS BEING CONSIDERED"
```

```
      PRINT*,"       ITMAX = ",ITMAX," = MAXIMUM NUMBER OF ITERATIONS",
     1" ALLOWED"
      PRINT*,"       NSIG = ",NSIG," = NUMBER OF SIGNIFICANT DIGIT ",
     1 "ACCURACY DESIRED"
      PRINT*,"         MW1 = ",MW1," = MOLECULAR WEIGHT OF COMPOUND # 1"
      PRINT*,"         MW2 = ",MW2," = MOLECULAR WEIGHT OF COMPOUND # 2"
      PRINT*,"      C1INM = ",C1INM," = INITIAL CONCENTRATION OF COMPOUND
     1 # 1 (MG/L)"
      PRINT*,"      C2INM = ",C2INM," = INITIAL CONCENTRATION OF COMPOUND
     1 # 2 (MG/L)"
      PRINT*,"FAC1    = ",FAC1
      PRINT*,"FAC2    = ",FAC2
      PRINT*,"Z1      = ",Z1
      PRINT*,"      NDATA = ",NDATA," = # OF DATA POINTS"
      PRINT*,"         NO = ",NO," = # OF DEPENDENT VARIABLES"
      PRINT*,"         NI = ",NI," = # OF INDEPENDENT VARIABLES"
      PRINT*,"       NPAR = ",NPAR," = # OF PARAMETERS REGRESSED"
      PRINT*,"       BETA = ",(BETA(I),I=1,NPAR)," THE INITIAL ",
     1"GUESSES OF THESE PARAMETERS"
      PRINT*,"      MAXITR = ",MAXITR," MAX. # OF ITERATIONS ALLOWED"
     1," IN RVEST"
      PRINT*,"        DEL = ",DEL
      PRINT*,"       NFIG = ",NFIG
      PRINT*,"       RLAM = ",RLAM
      PRINT*,"       FACT = ",FACT
```

PROGRAM MSIAS 73/730 OPT=2 FTN 4.8+587 85/07/30

```
      PRINT*,"       RLMAX = ",RLMAX
      PRINT*,"       RLMIN = ",RLMIN
      WRITE(6,5010)
 5010 FORMAT(" ",/////" ",2X," FREUNDLICH ISOTHERMS FOR THE FIRST "
     1,"COMPOUND ON A MASS BASIS"//)
      PRINT*,"         KK1 = ",KK1," = COEFFICIENT OF THE FREUNDLICH ADS
     1ORPTION ISOTHERM FOR COMPOUND # 1, IN TERMS OF MG/G"
      PRINT*,"         CC1P = ",CC1P," (MG/L) CONCENTRATION AT WHICH THE"
     1," SECOND FREUNDLICH ISOTHERM OF COMPOUND NO. 1 STARTS TO APPLY"
      PRINT*,"         KK1P = ",KK1P," COEFF. OF THE FREUNDLICH ISOTHERM ",
     1"( IN MGRAMS/GRAM) FOR THE SECOND RANGE OF COMPOUND NO.1"
      PRINT*,"         N1P = ",N1P," EXPONENT OF THE FREUNDLICH ISOTHERM",
     1" ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      WRITE(6,5020)
 5020 FORMAT(" ",/////" ",2X," FREUNDLICH ISOTHERMS FOR THE SECOND ",
     1"COMPOUND ON A MASS BASIS")
      PRINT*,"         KK2 = ",KK2," = COEFFICIENT OF THE FREUNDLICH ADS
     1ORPTION ISOTHERM FOR COMPOUND # 2, IN TERMS OF MG/G"
      PRINT*,"         N2 = ",N2," = EXPONENT OF THE FREUNDLICH ADSORPT
     1ION ISOTHERM FOR COMPOUND # 2"
      PRINT*,"         CC2P = ",CC2P," (MG/L) CONCENTRATION AT WHICH THE ",
     1"SECOND FREUNDLICH ISOTHERM OF COMPOUND NO. 2 STARTS TO APPLY"
      PRINT*,"         KK2P = ",KK2P," COEFFICIENT OF THE FREUNDLICH ISOTHERM
     1 ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
      PRINT*,"         N2P = ",N2P," EXPONENT OF THE FREUNDLICH ISOTHERM",
     2" ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      WRITE(6,5030)
 5030 FORMAT(" ",/////" ",2X,"THE LANGMUIR ISOTHERMS FOR THE FIRST ",
     1"COMPOUND ON A MASS BASIS"//)
      PRINT*,"         QM1A = ",QM1A," = COEFFICIENT OF THE LANGMUIR ADS
     1ORPTION ISOTHERM FOR COMPOUND # 1, IN TERMS OF MG/G"
      PRINT*,"         BB1 = ",BB1," = COEFFICIENT OF THE LANGMUIR"
     1," ISOTHERM , IN TERMS OF MG/G"
      PRINT*,"         CC1P = ",CC1P," (MG/L) CONCENTRATION AT WHICH THE ",
     1"SECOND LANGMUIR ISOTHERM OF COMPOUND NO. 1 STARTS TO APPLY"
      PRINT*,"         QM1MP = ",QM1MP," COEFFICIENT OF THE LANGMUIR ISOTHERM"
     1," ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      PRINT*,"         BB1P = ",BB1P," COEFFICIENT OF THE LANGMUIR ISOTHERM"
     1," ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      WRITE(6,5040)
 5040 FORMAT(" ",/////" ",2X," THE LANGMUIR ISOTHERMS FOR THE SECOND ",
     1" COMPOUND ON A MASS BASIS"//)
      PRINT*,"         QM2A = ",QM2A," = COEFFICIENT OF THE LANGMUIR ADS
     2ORPTION ISOTHERM FOR COMPOUND # 2, IN TERMS OF MG/G"
      PRINT*,"         BB2 = ",BB2," = COEFFICIENT OF THE LANGMUIR"
     1," ISOTHERM , IN TERMS OF MG/G"
      PRINT*,"         CC2P = ",CC2P," (MG/L) CONCENTRATION AT WHICH THE ",
     1"SECOND LANGMUIR ISOTHERM OF COMPOUND NO. 2 STARTS TO APPLY"
      PRINT*,"         QM2MP = ",QM2MP," COEFFICIENT OF THE LANGMUIR ISOTHERM"
     2," ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
      PRINT*,"         BB2P = ",BB2P," COEFFICIENT OF THE LANGMUIR ISOTHERM"
     2," ( IN MG/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
      WRITE(6,5050)
 5050 FORMAT(" ",/////" ",2X," THE FREUNDLICH ISOTHERMS FOR THE FIRST"
     1," COMPOUND ON A MOLAR BASIS"//)
      PRINT*,"         C1P = ",C1P," MOLAR CONCENTRATION AT WHICH THE"
     1," SECOND FREUNDLICH ISOTHERM OF COMPOUND NO. 1 STARTS TO APPLY"
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      PROGRAM MSIAS      73/730  OPT=2                          FTN 4.8+587        05/07/30.

            PRINT*,"              K1 = ",K1," = COEFFICIENT OF THE FREUNDLICH ADSO
           1RPTION ISOTHERM FOR COMPOUND # 1 , IN TERMS OF MMOLE/G"
            PRINT*,"              N1 = ",N1," = EXPONENT OF THE FREUNDLICH ADSORPT
      175   1ION ISOTHERM FOR COMPOUND # 1"
            PRINT*,"     K1P = ",K1P," COEFF. OF THE FREUNDLICH ISOTHERM ",
           1"( IN MMOLES/GRAM) FOR THE SECOND RANGE OF COMPOUND NO.1"
            PRINT*,"     N1P = ",N1P," EXPONENT OF THE FREUNDLICH ISOTHERM",
           1"  ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
      180   WRITE(6,5060)
           5060 FORMAT(" ",/////," ",2X," THE FREUNDLICH ISOTHERMS FO THE SECOND"
           1," COMPOUND ON A MOLAR BASIS"//)
            PRINT*,"              K2 = ",K2," = COEFFICIENT OF THE FREUNDLICH ADSO
           1RPTION ISOTHERM FOR COMPOUND # 2 , IN TERMS OF MMOLE/G"
      185   PRINT*,"              N2 = ",N2," = EXPONENT OF THE FREUNDLICH ADSORPT
           1ION ISOTHERM FOR COMPOUND # 2"
            PRINT*,"     C2P = ",C2P," MOLAR CONCENTRATION AT WHICH THE ",
           1"SECOND FREUNDLICH ISOTHERM OF COMPOUND NO.2 STARTS TO APPLY"
            PRINT*,"     K2P = ",K2P," COEFFICIENT OF THE FREUNDLICH ISOTHERM
      190   1  ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
            PRINT*,"     N2P = ",N2P," EXPONENT OF THE FREUNDLICH ISOTHERM",
           2"  ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
            WRITE(6,5070)
           5070 FORMAT(" ",/////," ",2X," THE LANGMUIR ISOTHERMS FOR THE FIRST ",
      195   1"COMPOUND ON A MOLAR BASIS"//)
            PRINT*,"     CO1P = ",CO1P," MOLAR CONCENTRATION AT WHICH THE ",
           1"SECOND LANGMUIR ISOTHERM OF COMPOUND NO. 1 STARTS TO APPLY"
            PRINT*,"              QM1 = ",QM1," = COEFFICIENT OF THE LANGMUIR ADSO
           1RPTION ISOTHERM FOR COMPOUND # 1 , IN TERMS OF MMOLE/G"
      200   PRINT*,"              B1 = ",B1," = COEFFICIENT OF THE LANGMUIR ADSORP
           1TION ISOTHERM FOR COMPOUND # 1 , IN LITERS/MILLIMOLE"
            PRINT*,"     QM1P = ",QM1P," COEFFICIENT OF THE LANGMUIR ISOTHERM"
           1,"  ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
            PRINT*,"     B1P = ",B1P," COEFFIENT OF THE LANGMUIR ISOTHERM"
      205   1," ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 1"
            WRITE(6,5080)
           5080 FORMAT(" ",/////," ",2X," THE LANGMUIR ISOTHERM FOR COMPOUND #2 ",
           1"ON A MOLAR BASIS"//)
            PRINT*,"     CO2P = ",CO2P," MOLAR CONCENTRATION AT WHICH THE ",
      210   1"SECOND LANGMUIR ISOTHERM OF COMPOUND NO. 2 STARTS TO APPLY"
            PRINT*,"              B2 = ",B2," = COEFFICIENT OF THE LANGMUIR ADSORP
           2TION ISOTHERM FOR COMPOUND # 2, IN LITERS/MILLIMOLE"
            PRINT*,"     QM2P = ",QM2P," COEFFICIENT OF THE LANGMUIR ISOTHERM"
      215   2,"  ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
            PRINT*,"     B2P = ",B2P," COEFFIENT OF THE LANGMUIR ISOTHERM"
           2," ( IN MMOLES/GRAM ) FOR THE SECOND RANGE OF COMPOUND NO. 2"
            WRITE(6,5090)
           5090 FORMAT(" ",/////////" ",2X,"THE VALUES OF PORE(I)"/)
            PORE(1)=KK1
      220   PORE(2)=K2
            PORE(3)=N1
            PORE(4)=N2
            PORE(5)=KK1P
            PORE(6)=K2P
      225   PORE(7)=N1P
            PORE(8)=N2P
            PORE(9)=CC1P-CFNON1
            PORE(10)=C2P
```

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      PROGRAM MSIAS      73/730  OPT=2                          FTN 4.8+587        05/07/30

            PORE(11)=CFNON1
      230   PRINT*,"PORE (1 TO 7) =",(PORE(IG),IG=1,7)
            PRINT*,"PORE (8 TO 14)=",(PORE(IG),IG=8,14)
            DO 9500 J=1,NDATA
             READ*,C1EXP(J),C2EXP(J),Q1EXP(J),Q2EXP(J),MEXP(J),VEXP(J),NUN(J)
           1,C1IN(J),C2IN(J)
      235     PRINT*,"
             VMLXP(J)=VEXP(J)/MEXP(J)
             PRINT*,"C1EXP(J)=",C1EXP(J)," Q1EXP(J)=",Q1EXP(J)," C2EXP(J)=",
           1C2EXP(J),"  Q2EXP(J)=",Q2EXP(J),"  MEXP(J)=",MEXP(J),"  VEXP(J)=",
           1VEXP(J)
      240   9500 CONTINUE
            WRITE(6,119)
            WRITE(6,120) TEST, COMP1, COMP2
            WRITE(6,555) C1INN, C2INN
            WRITE(6,230)
      245   C
            DO 9250 I=1,MP
             WRITE(6,200) C1EXP(I),C2EXP(I),Q1EXP(I),Q2EXP(I),VMEXP(I)
           9250 CONTINUE
            DO 500 J=1,NDATA
      250   C2EXP(J)=C2EXP(J)/MM2
            Q2EXP(J)=Q2EXP(J)/MM2
            C2IN(J)=C2IN(J)/MM2
            XX(3,J)=VMLXP(J)
            XX(1,J)=C1IN(J)-CFNON1
      255   XX(2,J)=C2IN(J)
            Y(1,J)=(C1EXP(J)-CFNON1)
            Y(2,J)=C2EXP(J)
           500 CONTINUE
            WRITE(6,119)
      260   119 FORMAT("1",18X,"EXPERIMENTAL DATA"////)
            WRITE(6,120) TEST,COMP1,COMP2
```

```
      120 FORMAT("0",15X,"EXPERIMENT # ",4(A10)//"0",15X,"COMPONENT # 1 = ",
     1 4(A10)/"0",15X,"COMPONENT # 2 = ",4(A10)//)
          WRITE(6,125) CC1IN, CC2IN
      125 FORMAT("  INITIAL CONCENTRATION OF COMPUND # 1 = ",E14.6,
     1       " MILLIMOLE / L"/
     2       " INITIAL CONCENTRATION OF COMPOUND # 2 = ",E14.6,
     4       " MILLIMOLE / L"//)
          WRITE(6,130)
      130 FORMAT("  ",6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",
     1       " = ",13X,"V/M",14X,"NUN"//
     1       " = ",13X,"M-MOLE/L",11X,"M-MOLE/L",9X,"M-MOLE/G",9X,
     1       "M-MOLE/G",9X,"LITERS/G"/)
C
          DO 150 I=1,NDATA
          WRITE(6,140) C1EXP(I),C2EXP(I),Q1EXP(I),Q2EXP(I),VMEXP(I),NUN(I)
      140 FORMAT("  ",5(E14.6,3X),3X,I3)
      150 CONTINUE
          WRITE(6,5100)
     5100 FORMAT("1",3X,"INPUT TO MVEST"//" ",1X,"X(1,I)",5X,
     1"X(2,I)",5X,"X(3,I)",5X,"Y(1,I)",5X,"Y(2,I)")
          DO 145 KLOP=1,NDATA
          PRINT*,XX(1,KLOP),XX(2,KLOP),XX(3,KLOP),Y(1,KLOP),Y(2,KLOP)
      145 CONTINUE
          WRITE(6,151)
```

```
PROGRAM MSIAS      73/730  OPT=2                          FTN 4.0+587        05/07/30

      151 FORMAT("1","START OF CALCULATIONS BASED ON A WIDE RANGE OF VALUES",
     1" OF V/M , TAKEN IN INCREASING ORDER"//)
          CALL MVEST(DEL,MFIG,NDATA,RLAM,FACT,RLMAX,RLMIN,MAXITR,MI
     1,NO,NPAR,BETA,Y,XX,PM,A,A1,P)
          C1P=CC1P/BETA(1)
          CC1IN=CC1INN/BETA(1)
          CMON1F=CFNCM1/BETA(1)
          WRITE(6,119)
          WRITE(6,120)
          WRITE(6,127) CC1IN, CC2IN
      127 FORMAT("  INITIAL CONCENTRATION OF COMPUND # 1 = ",E14.6,
     2       " MILLIMOLE / L"/
     3       " INITIAL CONCENTRATION OF COMPOUND # 2 = ",E14.6,
     4       " MILLIMOLE / L"//)
          WRITE(6,133)
      133 FORMAT("  ",6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",
     1       " = ",13X,"V/M",14X,"NUN"//
     1       " = ",13X,"M-MOLE/L",11X,"M-MOLE/L",9X,"M-MOLE/G",9X,
     1       "M-MOLE/G",9X,"LITERS/G"/)
          SUM=0.0
          DO 157 J=1,NDATA
          Q1EXP(J)=Q1EXP(J)/BETA(1)
          C1IN(J)=C1IN(J)/BETA(1)
          C1EXP(J)=C1EXP(J)/BETA(1)
          SUM=SUM+(A(1,J)**2)+(A(2,J)**2)
          WRITE(6,140) C1EXP(J),C2EXP(J),Q1EXP(J),Q2EXP(J),VMEXP(J),NUN(J)
          CC1=C1EXP(J)
          QC1=Q1EXP(J)
          CALL PLOTPT(CC1,QC1,18)
      157 CONTINUE
          WRITE(6,156) SUM
      156 FORMAT("1","////" ","SUM OF SQUARES OF THE CONC'S = ",E16.8)
          WRITE(6,5000)
          IF(NPAR.EQ.1) GO TO 158
          FAC1=1./(1.+ABS(BETA(1)))
          FAC2=1./(1.+ABS(BETA(2)))
      158 CONTINUE
          NN1=BETA(1)
          FRO=BETA(1)**(PORE(3)-1.)
          K1=PORE(1)*FRO
          K1P=PORE(5)*(BETA(1)**(PORE(7)-1.))
          PAR(8)=(C1INN-CFNCM1)/NN1
          PAR(9)=CC2IN
          PAR(6)=VMEXP(1)
          PAR(1)=(1.-FAC1)*K1
          PAR(2)=(1.-FAC2)*K2
          PAR(18)=FAC1*K1
          PAR(19)=FAC2*K2
          PAR(3)=N1
          PAR(4)=N2
          PAR(7)=N1P
          PAR(10)=(1.-FAC1)*K1P
          PAR(12)=FAC1*K1P
          PAR(14)=(CC1P-CFNCM1)/NN1
          PAR(20) = (PORE(3) + PORE(4)) / 2
          PAR(21) = (PORE(7) + PORE(4)) / 2
          PAR(22) = 1 / PAR(20)
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      PROGRAM MSIAS      73/730  OPT=2                                FTN 4.8+587        85/07/30

                  PAR(23) = 1 / PAR(21)
                  PAR(24) = SQRT(PAR(18) * PAR(19))
  345             PAR(25) = SQRT(PAR(12) * PAR(19))
                  PAR(11) = PAR(20) - 1
                  PAR(13) = PAR(21) - 1
                  PAR(15) = PAR(18) / PAR(24)
                  PAR(16) = PAR(19) / PAR(24)
  350             PAR(17) = PAR(12) / PAR(25)
                  PAR(26) = PAR(19) / PAR(25)
                  PAR(27) = PAR(24) ** (PAR(20) - PAR(22))
                  PAR(28) = PAR(25) ** (PAR(21) - PAR(23))
                  PRINT*,"PAR( 1 TO 7)= ",(PAR(IT),IT=1,7)
  355             PRINT*,"PAR(8 TO 14)= ",(PAR(IT),IT=8,14)
                  PRINT*,"PAR(15)=",PAR(15)," PAR(16)=",PAR(16)," PAR(17)=",PAR(17)
                  WRITE(6,151)
                  JC1=1
                  JC2=1
  360             JVM=1
                  DO 1175 J=1,100
                  IF(J.LE.5) PAR(5)=0.80010+(J-1)*0.0005
                  IF(J.GT.5.AND.J.LE.12) PAR(5)=PAR(5)+0.001
                  IF(J.GT.12.AND.J.LE.19) PAR(5)=PAR(5)+0.0025
  365             IF(J.GT.19.AND.J.LE.60) PAR(5)=PAR(5)+0.005
                  IF(J.GT.60.AND.J.LE.80) PAR(5)=PAR(5)+0.01
                  IF(J.GT.80) PAR(5)=PAR(5)+0.05
                  PAR(6)=0.5/PAR(5)
                  IF(J.GT.1) GO TO 1178
  370             CC1=0.99*CC1IN
                  QC1=0.9*(K1*CC1**N1)
                  X(1)=CC1IN-(QC1/PAR(6))
                  QC2=0.5*(K2*(0.99*CC2IN)**N2)
                  X(2)=CC2IN-(QC2/PAR(6))
  375             PRINT*,"PAR(1 TO 7) = ",(PAR(ILL),ILL=1,7)
                  PRINT*,"PAR(8 TO 13) = ",(PAR(ILL),ILL=8,13)
        1170      CONTINUE
                  WRITE(6,1172) (X(K),K=1,2),PAR(6)
  380     1172    FORMAT(" INITIAL X( )= ",9(E12.5,1X))
                  CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
                  VML(JJ)=PAR(6)
                  PRINT*,"J=",J," IER =",IER," FNORM=",FNORM," X(1)=",X(1)
                1," X(2)=",X(2)," VML(JJ)=",VML(JJ)
  385             QL1(J)=(PAR(6)-X(1))*VML(J)
                  QL2(J)=(CC2IN-X(2))*VML(J)
                   WRITE(6,57) X(1),QL1(J),X(2),QL2(J)
                   CL1(J)=X(1)+CAONIF
                  CL2(J)=X(2)
                  IF(J.EQ.1) GO TO 7000
                  IF(J.NE.25) GO TO 6750
                  PRINT*,"JC1=",JC1," JC2=",JC2," JVM=",JVM
                  PRINT*,"C1EXP(JC1)=",C1EXP(JC1),"  CL1(J)=",CL1(J),"  CL1(J-1)="
                1,CL1(J-1),"  JC1=",JC1
                  PRINT*,"C2EXP(JC2)=",C2EXP(JC2),"  CL2(J)=",CL2(J)
                1," CL2(J-1)=",CL2(J-1),"  JC2=",JC2
                  PRINT*,"VMEXP(JVM)=",VMEXP(JVM),"  VML(J)=",VML(J)
                1," VML(J-1)=",VML(J-1),"  JVM=",JVM
                  PRINT*,"X( )= ",(X(KOO),KOO=1,2)
        6750      CONTINUE
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      PROGRAM MSIAS      73/730  OPT=2                                FTN 4.8+587        85/07/30

  400             IF(JC1.GT.NP) GO TO 6800
                  IF(CL1(J).LT.C1EXP(JC1).AND.CL1(J-1).GE.C1EXP(JC1)) GO TO 6900
                  PRINT*,"AFTER 6750, JC1=",JC1,"  JC2=",JC2,"  JVM=",JVM
        6800      CONTINUE
  405             IF(JC2.GT.NP) GO TO 6810
                  IF(CL2(J).LT.C2EXP(JC2).AND.CL2(J-1).GE.C2EXP(JC2)) GO TO 6950
                   PRINT*,"AFTER 6800, JC1=",JC1,"  JC2=",JC2,"  JVM=",JVM
        6810      CONTINUE
                  IF(JVM.GT.NP) GO TO 7000
  410             IF(VML(J).LT.VMEXP(JVM).AND.VML(J-1).GE.VMEXP(JVM)) GO TO 6975
                  PRINT*,"AFTER 6810, JC1=",JC1,"  JC2=",JC2,"  JVM=",JVM
                  GO TO 7000
        6900      CONTINUE
        6905      CONTINUE
  415             XC1(JC1,2)=X(2)
                  XC1(JC1,1)=VML(J)
                  PRINT*,"J=",J,"  JC1=",JC1," XC1(JC1,1)=",XC1(JC1,1)
                  JC1=JC1+1
                  IF(JC1.GT.NP) GO TO 6800
```

```
      IF(JC1.GT.NP) GO TO 6800
      IF(C1EXP(JC1).GT.C1EXP(JC1-1)) GO TO 6980
      GO TO 6750
 6950 CONTINUE
      PRINT*,"J=",J," JC2=",JC2
 6955 CONTINUE
      XC2(JC2,1)=X(1)
      XC2(JC2,2)=VML(J)
      PRINT*,"J=",J," JC2=",JC2," XC2(JC2,2)=",XC2(JC2,2)
      JC2=JC2+1
      IF(JC2.GT.NP) GO TO 6810
      IF(C2EXP(JC2).GT.C2EXP(JC2-1)) GO TO 6950
      GO TO 6800
 6975 CONTINUE
      PRINT*,"J=",J," JVM=",JVM
      DO 6980 KITE=1,2
      XVM(JVM,KITE)=X(KITE)
 6980 CONTINUE
      PRINT*,"J=",J," JVM=",JVM," XVM(JVM,1)=",XVM(JVM,1)
      JVM=JVM+1
      IF(JVM.GT.NP) GO TO 7000
      IF(VMEXP(JVM).GT.VMEXP(JVM-1)) GO TO 6975
      GO TO 6810
 7000 CONTINUE
      PRINT*,"WENT BY 7000"
 1175 CONTINUE
      NPOT=J
      IF(NPOT.GT.100) NPOT=100
      PRINT*,"JC1=",JC1," JC2=",JC2,"   JVM=",JVM," NPOT=",NPOT
      NPP=JC1
      IF(JC2.LT.NPP) NPP=JC2
      IF(JVM.LT.NPP) NPP=JVM
      NPP=NPP-1
      PRINT*,"NPP=",NPP," JC1=",JC1," JC2=",JC2," JVM=",JVM
      PRINT*," MATRIX XC1"
      DO 7100 KOOL=1,NPP
      PRINT*,(XC1(KOOL,KIK),KIK=1,2)
 7100 CONTINUE
C
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PROGRAM MSIAS      73/738  OPT=2                    FTN 4.8+587      85/07/30

      WRITE(6,100)
      WRITE(6,104)
      WRITE(6,120) TEST,COMP1,COMP2
      WRITE(6,125) CC1IN,CC2IN
      WRITE(6,128)
  128 FORMAT(" ",///" ",73X,"GIVEN"/)
      WRITE(6,131)
  131 FORMAT(" "  ,6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",
     1       "  ",13X,"V/M**3"//
     1       "  ",2X,"M-MOLE/L",11X,"M-MOLE/L",9X,"M-MOLE/G",9X,
     1       "M-MOLE/G",9X,"LITERS/G"/)
  132 FORMAT(" "  ,6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",
     1       "  ",13X,"Q-1",14X,"Q-2",13X,"V/M**3",12X,"V/M**3"//
     1       "  ",2X,"M-MOLE/L",11X,"M-MOLE/L",9X,"M-MOLE/G",9X,
     1       "M-MOLE/G",9X,"M-MOLE/G",9X,"M-MOLE/G",9X,"LITERS/G",
     1       7X,"LITERS/G"/)
      DO 2150 I=1,NPOT
      WRITE(6,200) CL1(I),CL2(I),QL1(I),QL2(I),VML(I)
      CC1=CL1(I)
      QLL1=QL1(I)
      CC1A=CC1-CNON1F
      QPURE1=K1*CC1A**N1
      IF(CC1A.GT.PAR(14)) QPURE1=K1P*CC1A**N1P
      CALL PLOTPT(CC1,QLL1,9)
      CALL PLOTPT(CC1,QPURE1,4)
 2150 CONTINUE
      WRITE(6,25)
   25 FORMAT("1","START OF CALCULATIONS BASED ON THE EXPERIMENTAL =
     1,"VALUES OF C1")

      SUMSQ=0.0
      REDSUM=0.0
      DO 1500 J=1,NPP
      PAR(8)=C1IN(J)-CNON1F
      PAR(9)=C2IN(J)
      PAR(5)=C1EXP(J)-CNON1F
      DO 26 KITE=1,2
      X(KITE)=XC1(J,KITE)
   26 CONTINUE
      KK=1
         WRITE(6,30)KK,X(KK)
         DO 32 KK=2,N
         WRITE(6,29)KK,X(KK)
   32 CONTINUE
      PRINT*,"   PAR = ",(PAR(KT),KT=1,7)
C
C     CALL ZSPOW(FCN1,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)

      PRINT*,"IER=",IER," X(1)=",X(1)," X(2)=",X(2)
      WRITE(6,31)
      Q01(J)=(PAR(8)-PAR(5))*X(1)
      Q02(J)=(PAR(9)-X(2))*X(1)
   78 CONTINUE
      CF1(J)=C1EXP(J)
      CF2(J)=X(2)
      VMF(J)=X(1)
      SUMSQ=SUMSQ+(Q1EXP(J)-Q01(J))**2
```

```
      PROGRAM MSIAS      73/730  OPT=2                              FTN 4.8+587        85/07/30

                  REDSUM=REDSUM+(1.-QQ1(J)/Q1EXP(J))**2
  1500 CONTINUE
       PRINT*,' SUM OF SQUARES =',SUMSQ
       PRINT*,' REDUCED SUM = ',REDSUM
       SUMSQM=SUMSQ*(MW1**2)
C
       WRITE(6,100)
  100 FORMAT(' ','  IT USES THE TWO MASS BALANCES AND REQUIRES THE '
     1,'INITIAL LIQUID PHASE CONCENTRATIONS'/' ','  OF BOTH COMPONENTS'
     2,' AND EQUILIBRIUM LIQUID PHASE CONCENTRATION OF COMPONENT NO. 1',
     3//)
       WRITE(6,120) TEST,COMP1,COMP2
       WRITE(6,125) CC1IN, CC2IN
       WRITE(6,129)
  129 FORMAT(' ',3X,'EXPERIMENTAL',55X,'EXPERIMENTAL',5X,'EXPERIMENTAL',
     1 21X,'EXPERIMENTAL'/)
       WRITE(6,132)
C
       DO 3150 I=1,NPP
          WRITE(6,200) CF1(I),CF2(I),QQ1(I),QQ2(I),Q1EXP(I)
     1,Q2EXP(I),VMF(I),VMEXP(I)
          CC1=CF1(I)
          QC1=QQ1(I)
          CALL PLOTPT(CC1,QC1,2)
 3150 CONTINUE
       WRITE(6,3151)
 3151 FORMAT('1',' START OF CALCULATIONS BASED ON THE EXPERIMENTAL '
     1,'VALUES OF C2'///)
       DO 5000 J=1,NPP
       PAR(8)=C1IN(J)-CNONIF
       PAR(9)=C2IN(J)
       PAR(6)=C2EXP(J)
       DO 526 KITE=1,2
       X(KITE)=XC2(J,KITE)
  526  CONTINUE
       KK=1
          WRITE(6,30)KK,X(KK)
          DO 532 KK=2,N
             WRITE(6,29)KK,X(KK)
  532     CONTINUE
          PRINT*,'    PAR = ',(PAR(KT),KT=1,7)
C
C        CALL ZSPOW(FCN2,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)

       QQ1(J)=(PAR(8)-X(1))*X(2)
       QQQ2(J)=(PAR(9)-C2EXP(J))*X(2)
          PRINT*,'IER=',IER,'  X(1)=',X(1),'  X(2)=',X(2)
          WRITE(6,31)
       WRITE(6,577) X(1),QQ1(J),C2EXP(J),QQQ2(J),X(2)
          CF1(J)=X(1)+CNONIF
          CFF2(J)=C2EXP(J)
          VMF(J)=X(2)
          SUMSQ=SUMSQ+(Q2EXP(J)-QQQ2(J))**2
       SUMSQM=SUMSQM+(Q2EXP(J)-QQQ2(J))*MW2)**2
          REDSUM=REDSUM+(1.-QQQ2(J)/Q2EXP(J))**2
  5000 CONTINUE
       WRITE(6,100)
```

```
      PROGRAM MSIAS      73/730  OPT=2                              FTN 4.8+587        85/07/30

       WRITE(6,107)
  107 FORMAT(' ','  IT USES THE TWO MASS BALANCES AND REQUIRES THE '
     1,'INITIAL LIQUID PHASE CONCENTRATIONS'/' ','  OF BOTH COMPONENTS'
     2,' AND EQUILIBRIUM LIQUID PHASE CONCENTRATION OF COMPONENT NO. 2',
     3//)
       WRITE(6,120) TEST,COMP1,COMP2
       WRITE(6,125) CC1IN, CC2IN
       WRITE(6,1128)
 1128 FORMAT(' ',17X,'EXPERIMENTAL',41X,'EXPERIMENTAL',5X,'EXPERIMENTAL',
     1 18X,'EXPERIMENTAL'/)
       WRITE(6,132)
C
       DO 1150 I=1,NPP
          WRITE(6,200) CF1(I),CFF2(I),QQ1(I),QQQ2(I),Q1EXP(I)
     1,Q2EXP(I),VMF(I),VMEXP(I)
 1150 CONTINUE
       WRITE(6,2151) NPP,SUMSQ,REDSUM
 2151 FORMAT(' '/////' ',5X,'SUMS OF SQUARES OF Q1 AND Q2 IN M-MOLE/G'
     1,' BASED ON ',I3,' POINTS'//' '
     1,'SUM OF SQUARES = ',E14.6//' ','REDUCED SUM OF THE REDUCED '
     2,'SQUARES = ',E14.6///)
       WRITE(6,2149) NPP,SUMSQM
 2149 FORMAT(' '/////' ',5X,'SUMS OF SQUARES OF Q1 AND Q2 IN M-GRAM/G'
     1,' BASED ON ',I3,' POINTS'//' '
     1,'SUM OF SQUARES = ',E14.6////////)
```

```
      WRITE(6,2152)
 2152 FORMAT('1',' START OF CALCULATIONS BASED ON THE EXPERIMENTAL"
     1,' VALUES OF W/M')
  600 CSUMSQM=0.0
      CSUMSQ=0.0
      CREDSUM=0.0
      DO 6000 J=1,NPP
      PAR(8)=C1IN(J)-CMON1F
  605 PAR(9)=C2IN(J)
      PAR(5)=MEXP(J)
      PAR(6)=VEXP(J)/MEXP(J)
      DO 6526 KITE=1,2
      X(KITE)=XVM(J,KITE)
 6526 CONTINUE
  610 KK=1
         WRITE(6,30)KK,X(KK)
         DO 6532 KK=2,N
            WRITE(6,29)KK,X(KK)
 6532    CONTINUE
  615 PRINT*,'    PAR = ',(PAR(KT),KT=1,7)
C
C     CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,X,FNORM,WK,IER)
C
  620 PRINT*,"IER=",IER," X(1)=",X(1)," X(2)=",X(2)
      WRITE(6,31)
      VMF(J)=PAR(6)
      QQ1(J)=(PAR(8)-X(1))*VMF(J)
      QQQ2(J)=(PAR(9)-X(2))*VMF(J)
  625 WRITE(6,57) X(1),QQ1(J),X(2),QQQ2(J),VMF(J)
         CFF1(J)=X(1)+CMON1F
         CFF2(J)=X(2)
      CSUMSQ=CSUMSQ+(C1EXP(J)-X(1))**2+(C2EXP(J)-X(2))**2
```

```
PROGRAM MSIAS      73/730  OPT=2                                FTN 4.8+587        85/07/3C
      CREDSUM=CREDSUM+(1.-X(1)/C1EXP(J))**2+(1.-X(2)/C2EXP(J))**2
  630 CSUMSQM=CSUMSQM+((C1EXP(J)-X(1))*MW1)**2+
     1          ((C2EXP(J)-X(2))*MW2)**2
 6000 CONTINUE
      WRITE(6,100)
      WRITE(6,104)
  635 104 FORMAT('-',' IT USES THE TWO MASS BALANCES AND REQUIRES THE -
     1,'INITIAL LIQUID PHASE CONCENTRATIONS'/' ',' OF BOTH COMPONENTS"
     2,' AND THE ACTIVATED CARBON CONCENTRATION'///)
      WRITE(6,120) ICST,COMP1,COMP2
      WRITE(6,125) CC1IN, CC2IN
  640 WRITE(6,128)
 6128 FORMAT('-',70X,"EXPERIMENTAL",5X,"EXPERIMENTAL",
     1104X,"EXPERIMENTAL"/)
      WRITE(6,132)
C
  645 DO 6150 I=1,NPP
         WRITE(6,2001) CFF1(I),CFFZ(I),QQ1(I),QQQ2(I),Q1EXP(I)
     1,Q2EXP(I),VMF(I),VMEXP(I)
 6150 CONTINUE
      WRITE(6,152) NPP,CSUMSQ,CREDSUM
  650 152 FORMAT('1','////'-',5X,"SUMS OF SQUARES OF C1 AND C2 IN M-MOLES/L"
     1," BASED ON ",I3," POINTS"/"-",
     1"SUM OF SQUARES = ",E14.6//" &","REDUCED SUM OF THE REDUCED "
     2,"SQUARES = ",E14.6///)
      WRITE(6,149) NPP,CSUMSQM
  655 149 FORMAT('-'////'-',5X,"SUMS OF SQUARES OF C1 AND C2 IN M-GRAMS/L"
     1," BASED ON ",I3," POINTS"/"-",
     1"SUM OF SQUARE = ",E14.6///////)
C
      WRITE(6,1805)
  660 1805 FORMAT('1'////" THE FIRST GRAPH PRESENTS THE ISOTHERMS OF",
     2       " COMPONENT # 1 AND THE SECOND GRAPH PRESENTS",
     3       " THE ISOTHERMS OF COMPONENT # 2"///)
C
      WRITE(6,1810)
  665 1810 FORMAT(' ',' LEGEND OF GRAPH BELOW'/,
     2       " ---------------------"/,
     3       " 1 = PREDICTED MULTICOMPONENT ISOTHERM"/,
     4       " 0 = OBSERVED MULTICOMPONENT ISOTHERM"/,
     5       " * = SINGLE COMPONENT ISOTHERM")
  670 C
C     200 FORMAT(" ",6(E14.6,3X),E14.6,1X,E14.6)
      CALL OUTPLT
C
  675 DO 220 I=1,NP
         CC2=C2EXP(I)
         QCC2=Q2EXP(I)
         CALL PLOTPT(CC2,QCC2,18)
  220 CONTINUE
      DO 2220 I=1,180
  680 CC2=CL2(I)
      QC2=QL2(I)
      QPURE2=K2*CC2**N2
      CALL PLOTPT(CC2,QC2,9)
      CALL PLOTPT(CC2,QPURE2,4)
```

```
      PROGRAM MSIAS      73/730  OPT=2                    FTN 4.8+587        85/87/3

685          2220 CONTINUE
                  CALL OUTPLT
               C
                  WRITE(6,100)
                  WRITE(6,120) TEST, COMP1, COMP2
690               WRITE(6,225) C1INM, C2INM
           225 FORMAT(" INITIAL CONCENTRATION OF COMPOUND # 1 = ",E14.6,
                 2       " MILLIGRAM / L",//
                 3       " INITIAL CONCENTRATION OF COMPOUND # 2 = ",E14.6,
                 4       " MILLIGRAM / L"////)
695               WRITE(6,230)
           230 FORMAT(" ",6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",
                 1      13X,"V/M"//
                 1" ",3X,"MILLIG/L",11X,"MILLIG/L",9X,"MILLIG/G",9X,"MILLIG/G",
                 1 6X,"LITERS/G"//)
700            C
                  DO 250 I=1,NP
                     CC1=C1EXP(I)*C1EXP(I)*MW1
                     CC2=C2EXP(I)*C2EXP(I)*MW2
                     Q1EXP(I)=Q1EXP(I)*MW1
705                  Q2EXP(I)=Q2EXP(I)*MW2
                     QE1=Q1EXP(I)
                     CALL PLOTPT(CC1,QE1,2)
                     WRITE(6,200) CC1,CC2,QE1,Q2EXP(I),VMEXP(I)
           250 CONTINUE
710               WRITE(6,100)
                  WRITE(6,120)  TEST, COMP1, COMP2
                  WRITE(6,225)  C1INM, C2INM
                  WRITE(6,120)
                  WRITE(6,231)
715        231 FORMAT(" ",6X,"C-1",16X,"C-2",13X,"Q-1",14X,"Q-2",13X,"V/M"////
                 1" ",3X,"MILLIG/L",11X,"MILLIG/L",9X,"MILLIG/G",9X,"MILLIG/G"
                 2,11X,"LITERS/G"//)
                  DO 2250 I=1,100
720               CC1=CL1(I)*CL1(I)*MW1
                  QC1=QL1(I)*MW1
                  CC1A=CC1-CFNON1
                  QCC1=KK1*CC1A**N1
                  IF(CC1.GT.CC1P) QCC1=KK1P*CC1A**N1P
                  QL2(I)=QL2(I)*MW2
725               CL2(I)=CL2(I)*MW2
                  CALL PLOTPT(CC1,QC1,9)
                  CALL PLOTPT(CC1,QCC1,4)
                  WRITE(6,200)CC1,CL2(I),QC1,QL2(I),VML(I)
730        2250 CONTINUE
               C
                  CALL OUTPLT
               C
                  DO 260 I=1,NP
                     CC2=C2EXP(I)
735                  QCC2=Q2EXP(I)
                     CALL PLOTPT(CC2,QCC2,10)
           260 CONTINUE
                  DO 2260 I=1,100
                  CC2=CL2(I)
740               QC2=QL2(I)
                  QCC2=KK2*CC2**N2
                  CALL PLOTPT(CC2,QC2,9)
                  CALL PLOTPT(CC2,QCC2,4)
745        2260 CONTINUE
               C
                  CALL OUTPLT
                  FORMAT(" ",
                  FORMAT("0"," INITIAL GUESSES OF X(",I2,") = ",E14.6)
                  FORMAT(" ",11X,8H"C1",7X,"Q1",
750               1   8X,"C2",11X,"Q2",9X,"V/M"/
                  FORMAT(" ",6(1PE13.4,1X))
           100 FORMAT("1",10X,"PREDICTIVE PRELIMINARY ISOTHERM CALCULATIONS BASED
                 1 ON THE MSCAM COMPETITIVE ISOTHERM MODEL"//)
755               PRINT*," KK1P=",KK1P," N1P=",N1P," CFNON1=",CFNON1
                  TH(1)=KK1
                  TH(2)=N1
                  TH(3)=999.
                  NPROB=2
760               NOB=NP
                  TH(4)=KK1P
                  TH(5)=N1P
                  CNON=CFNON1
                  COIV=CC1P
765               CALL ISOPLOT(NPROB,TH,C1EXP,Q1EXP,CL1,QL1,NOB,NP,NUN,
                 1CNON,COIV,NPCT)
                  TH(1)=KK2/((1000.0)**N2)
                  TH(2)=N2
                  TH(3)=999.
770               DO 3000 I=1,NP
           3000 C2EXP(I)=C2EXP(I)*1000.0
                  DO 3010 I=1,100
           3010 CL2(I)=CL2(I)*1000.0
                  NPROB=2
775               TH(1)=KK2P/(1000.0**N2P)
                  TH(2)=N2P
                  CNON=0.00
                  COIV=CC2P
                  NOB=NP
780               CALL ISOPLOT(NPROB,TH,C2EXP,Q2EXP,CL2,QL2,NOB,NP,NUN,
                 1CNON,COIV,NPCT)
                  CALL PLOT(6.0,5.0,999)
                  STOP
                  END
```

```
SUBROUTINE FCN2       73/730  OPT=2                    FTN 4.8+587        85/07/30

      1               SUBROUTINE FCN2(G,F,N,PAR)
                      INTEGER N
                      REAL G(N),F(N),PAR(30)
                      IF(G(1).GT.0.0.AND.PAR(6).GT.0.0) GO TO 5
      5               PRINT* ,"                G(1)=",G(1)," PAR(6)=",PAR(6)
                    5 CONTINUE
                      IF(G(1).GT.PAR(14)) GO TO 20
                      TERM = (((PAR(15)*G(1)**PAR(3) + PAR(16)*PAR(6)**PAR(4))
                     1        ** PAR(22)) ** PAR(11))
     10               F(1) = (PAR(8)-G(1))*G(2) - PAR(1)*G(1)**PAR(3)
                     1       - TERM*((PAR(18)*G(1)**PAR(3))
                     2       ** PAR(22)) * PAR(27)
                      F(2) = (PAR(9)-PAR(6))*G(2) - PAR(2)*PAR(6)**PAR(4)
                     1       - TERM*((PAR(19)*PAR(6)**PAR(4))
     15              2       ** PAR(22)) * PAR(27)
                      GO TO 40
                    C
                     20 TERM = (((PAR(17)*G(1)**PAR(7) + PAR(26)*PAR(6)**PAR(4))
                     1        ** PAR(23)) ** PAR(13))
     20               F(1) = (PAR(8)-G(1))*G(2) - PAR(18)*G(1)**PAR(7)
                     1       - TERM*((PAR(12)*G(1)**PAR(7))
                     2       ** PAR(23)) * PAR(28)
                      F(2) = (PAR(9)-PAR(6))*G(2) - PAR(2)*PAR(6)**PAR(4)
     25              1       - TERM*((PAR(19)*PAR(6)**PAR(4))
                     2       ** PAR(23)) * PAR(28)
                    C
                     40 CONTINUE
                      RETURN
                      END
```

```
SUBROUTINE FCN1       73/730  OPT=2                    FTN 4.8+587        85/07/30

      1               SUBROUTINE FCN1(G,F,N,PAR)
                      INTEGER N
                      REAL G(N),F(N),PAR(30)
                      IF(PAR(5).GT.0.0.AND.G(2).GT.0.0) GO TO 5
      5               PRINT* ,"                PAR(5)=",PAR(5)," G(2)=",G(2)
                    5 CONTINUE
                      IF(PAR(5).GT.PAR(14)) GO TO 20
                      TERM = (((PAR(15)*PAR(5)**PAR(3) + PAR(16)*G(2)**PAR(4))
                     1        ** PAR(22)) ** PAR(11))
     10               F(1) = (PAR(8)-PAR(5))*G(1) - PAR(1)*PAR(5)**PAR(3)
                     1       - TERM*((PAR(18)*PAR(5)**PAR(3))
                     2       ** PAR(22)) * PAR(27)
                      F(2) = (PAR(9)-G(2))*G(1) - PAR(2)*G(2)**PAR(4)
     15              1       - TERM*((PAR(19)*G(2)**PAR(4))
                     2       ** PAR(22)) * PAR(27)
                      GO TO 40
                    C
                     20 TERM = (((PAR(17)*PAR(5)**PAR(7) + PAR(26)*G(2)**PAR(4))
                     1        ** PAR(23)) ** PAR(13))
     20               F(1) = (PAR(8)-PAR(5))*G(1) - PAR(18)*PAR(5)**PAR(7)
                     1       - TERM*((PAR(12)*PAR(5)**PAR(7))
                     2       ** PAR(23)) * PAR(28)
                      F(2) = (PAR(9)-G(2))*G(1) - PAR(2)*G(2)**PAR(4)
     25              1       - TERM*((PAR(19)*G(2)**PAR(4))
                     2       ** PAR(23)) * PAR(28)
                    C
                     40 CONTINUE
                      RETURN
                      END
```

```
SUBROUTINE FCN        73/730  OPT=2                    FTN 4.8+587        85/07/30

      1               SUBROUTINE FCN(G,F,N,PAR)
                      INTEGER N
                      REAL G(N),F(N),PAR(30)
                      IF(G(1).GT.0.0.AND.G(2).GT.0.0) GO TO 5
      5               PRINT* ,"                G(1)=",G(1)," G(2)=",G(2)
                    5 CONTINUE
                      IF(G(1).GT.PAR(14)) GO TO 20
                      TERM = (((PAR(15)*G(1)**PAR(3) + PAR(16)*G(2)**PAR(4))
                     1        ** PAR(22)) ** PAR(11))
     10               F(1) = (PAR(8)-G(1))*PAR(6) - PAR(1)*G(1)**PAR(3)
                     1       - TERM*((PAR(18)*G(1)**PAR(3))
                     2       ** PAR(22)) * PAR(27)
                      F(2) = (PAR(9)-G(2))*PAR(6) - PAR(2)*G(2)**PAR(4)
     15              1       - TERM*((PAR(19)*G(2)**PAR(4))
                     2       ** PAR(22)) * PAR(27)
                      GO TO 40
                    C
                     20 TERM = (((PAR(17)*G(1)**PAR(7) + PAR(26)*G(2)**PAR(4))
     20              1        ** PAR(23)) ** PAR(13))
                      F(1) = (PAR(8)-G(1))*PAR(6) - PAR(18)*G(1)**PAR(7)
                     1       - TERM*((PAR(12)*G(1)**PAR(7))
                     2       ** PAR(23)) * PAR(28)
                      F(2) = (PAR(9)-G(2))*PAR(6) - PAR(2)*G(2)**PAR(4)
     25              1       - TERM*((PAR(19)*G(2)**PAR(4))
                     2       ** PAR(23)) * PAR(28)
                    C
                     40 CONTINUE
                      RETURN
                      END
```

```
      SUBROUTINE MODEL(Y,XX,BETA,NPAR,A,NDATA,NI,NO)
      DIMENSION BETA(3),Y(NO,NDATA),XX(NI,NDATA),A(NO,NDATA)
      DIMENSION WK(300),PAR(30),F(3),G(2)
      REAL K1,K1P,FNORM
      COMMON /POW/ NSIG,N,ITMAX,PORE(31),FAC1,FAC2,Z1
      COMMON /DATA/ Q1EXP(31),Q2EXP(31),NUN(31)
      EXTERNAL FCN
      IF(NPAR.EQ.1) GO TO 20
      FAC1=1./(1.+(ABS(BETA(3))))
      FAC2=1./(1.+ABS(BETA(2)))
   20  CONTINUE
      FRO=BETA(1)**(PORE(3)-1.)
      K1=PORE(1)*FRO
      K1P=PORE(5)*(BETA(1)**(PORE(7)-1.))
      PAR(1)=(1.-FAC1)*K1
      PAR(2)=(1.-FAC2)*PORE(2)
      PAR(18)=FAC1*K1
      PAR(19)=FAC2*PORE(2)
      PAR(3)=PORE(3)
      PAR(4)=PORE(4)
      PAR(7)=PORE(7)
      PAR(10)=(1.-FAC1)*K1P
      PAR(12)=FAC1*K1P
      PAR(14)=PORE(9)/BETA(1)
      PAR(20) = (PORE(3) + PORE(4)) / 2
      PAR(21) = (PORE(7) + PORE(4)) / 2
      PAR(22) = 1 / PAR(20)
      PAR(23) = 1 / PAR(21)
      PAR(24) = SQRT(PAR(18) * PAR(19))
      PAR(25) = SQRT(PAR(12) * PAR(19))
      PAR(11) = PAR(20) - 1
      PAR(13) = PAR(21) - 1
      PAR(15) = PAR(18) / PAR(24)
      PAR(16) = PAR(19) / PAR(24)
      PAR(17) = PAR(12) / PAR(25)
      PAR(26) = PAR(19) / PAR(25)
      PAR(27) = PAR(24) ** (PAR(20) - PAR(22))
      PAR(28) = PAR(25) ** (PAR(21) - PAR(23))
      PRINT*," FAC1 = ",FAC1," FAC2=",FAC2," MW1=",BETA(1)
      DO 100 I=1,NDATA
       PAR(8)=XX(1,I)/BETA(1)
      PAR(9)=XX(2,I)
       G(1)=Y(1,I)/BETA(1)
       G(2)=Y(2,I)
      PAR(6)=XX(3,I)
      CALL ZSPOW(FCN,NSIG,N,ITMAX,PAR,G,FNORM,WK,IER)
      IF(IER.NE.0) PRINT*,"IER=",IER," I=",I," FNORM=",FNORM,
     1" G(1)=",G(1)," G(2)=",G(2)
      A(1,I)=Y(1,I)-G(1)*BETA(1)
      A(2,I)=Y(2,I)-G(2)
  100    CONTINUE
      RETURN
      END
```

APPENDIX II

COLUMN DATA

II.1 BASIC INFORMATION

Column Internal Radius	= 0.95 cm
Height of GAC in Column	= 12.7 cm
Height of Sand on top of GAC	= 2.95 cm
Carbon Type	= Filtrasorb F-400
Carbon Mass	= 3.92634 g
GAC and Sand Particle Size	= 0.0297 to 0.0420 cm (40 - 50 mesh)
Approximate Flowrate	= 2 ml/min
Apparent Particle Density	= 0.75 g/cm^3

11.2 TCEA CONCENTRATIONS

	GAC COLUMN			CONTROL COLUMN		
	FLOWRATE (ML/MIN)	CONC. (MG/L)	TIME (MIN)	TIME (MIN)	CONC. (MG/L)	FLOWRATE (ML/MIN)
1	1.953600	0.000	242.			
2	1.953600	0.000	1230.	243.	.380	2.033900
3	1.945300	0.000	2659.	1232.	.392	2.033900
4	1.888300	0.000	4051.	2659.	.390	2.012800
5	1.766400	0.000	5500.	4061.	.375	2.033800
6	1.766400	0.000	5743.	5507.	.395	2.092600
7	1.766400	0.000	5906.			
8	1.812200	0.000	6988.	5912.	.383	2.092600
9	1.726400	0.000	8443.			
10	1.748900	0.000	9811.	8455.	.391	1.641400
11	1.625000	0.000	11255.	9813.	.385	1.824800
12	2.000100	0.000	12942.			
13	2.014900	0.000	14218.	12951.	.338	2.107500
14	2.014900	0.000	14503.	14261.	.336	2.127400
15	2.002600	0.000	15686.			
16	2.000900	0.000	17052.	15692.	.323	2.123700
17	2.000900	0.000	17421.	17065.	.322	2.111100
18	1.974300	0.000	18366.	17417.	.318	2.111100
19	1.974300	0.000	18646.	18375.	.316	2.081700
20	1.990600	0.000	19813.	18658.	.309	2.081700
21	2.052400	0.000	20145.	19822.	.298	2.052400
22	2.052400	0.000	20474.			
23	1.936700	0.000	21278.	20479.	.292	1.990600
24	1.936700	0.000	21584.	21281.	.290	2.081100
25	1.936700	0.000	21771.			
26	1.879500	0.000	22794.	21784.	.434	2.081100
27	1.879500	0.000	23037.	22805.	.437	2.028900
28	1.879500	0.000	23169.			
29	1.867300	0.000	24213.	23181.	.461	2.028900
30	1.867300	0.000	24490.	24226.	.444	2.056800
31	1.867300	0.000	24603.			
32	1.747600	0.000	25881.	24595.	.446	2.056800
33	1.747600	0.000	26042.			
34	1.845000	0.000	27030.	26042.	.453	2.045400
35	1.845000	0.000	27328.	27041.	.489	1.977300
36	1.845000	0.000	27473.	27329.	.464	1.977300
37	1.731400	0.000	28463.	27485.	.466	1.977300
38	1.731400	0.000	28756.	28482.	.481	2.072500
39	1.731400	0.000	28913.	28775.	.490	2.072500
40	1.685600	0.000	29894.	28921.	.489	2.072500
41	1.685600	0.000	30173.	29913.	.484	2.034700
42	1.685600	0.000	30355.	30194.	.467	2.034700
43	1.893000	0.000	31316.	30356.	.455	2.034700
44	1.893000	0.000	31616.	31329.	.466	2.047100
45	1.893000	0.000	31826.	31645.	.437	2.047100
46	2.095000	0.000	32635.	31826.	.430	2.047100
47	2.095000	0.000	33063.	32638.	.441	1.983200
48	2.095000	.000	33241.			
49	2.191200	.001	34368.	33236.	.398	1.983200
50	2.191200	.001	34594.	34370.	.395	2.075500
				34597.	.392	2.075500

	----- GAC COLUMN ------			--- CONTROL COLUMN ----		
	FLOWRATE	CONC.	TIME	TIME	CONC.	FLOWRATE
51	2.274400	.003	35676.	35679.	.420	2.024300
52	2.274400	.004	35959.	35951.	.411	2.024300
53	2.274400	.004	36094.	36085.	.411	2.024300
54	2.178600	.008	37105.	37106.	.411	2.040400
55				37405.	.409	2.040400
56	2.178600	.017	38541.	38544.	.404	2.039400
57	2.178600	.019	38886.	38682.	.408	2.039400
58	2.178800	.021	39006.	39001.	.436	2.039400
59	2.233600	.033	39999.	39998.	.459	1.983200
60	2.233600	.037	40275.	40271.	.484	1.983200
61	2.233600	.042	40462.	40464.	.476	1.983200
62	2.233600	.041	40589.	40579.	.476	1.983200
63	2.208200	.049	41413.	41415.	.498	2.003700
64	2.208200	.044	41717.	41718.	.488	2.003700
65	2.208200	.051	41933.	41925.	.491	2.003700
66	2.180000	.060	42907.	42913.	.489	1.968900
67	2.180000	.075	43302.			
68	2.119200	.094	44388.			
69	2.119200	.114	44779.	44774.	.498	1.990500
70	2.095800	.133	45767.	45771.	.501	1.952900
71	2.095800	.148	46186.	46180.	.502	1.952900
72	2.028800	.196	47171.	47174.	.491	1.872100
73	2.028800	.191	47468.	47462.	.484	1.872100
74	2.029600	.202	47635.	47629.	.480	1.872100
75	2.006600	.211	48619.	48619.	.485	1.814300
76	2.006600	.216	48998.	48996.	.491	1.814300
77	2.006800	.208	49290.	49282.	.504	1.814300
78	1.965700	.225	50058.	50056.	.471	1.695400
79	1.965000	.252	50382.	50386.	.471	1.110000
80	2.008450	.280	51505.	51511.	.495	2.052300
81	2.008450	.331	51960.	51953.	.505	2.052300
82	2.030100	.343	53094.	53091.	.499	2.025000
83	2.037140	.363	53460.	53450.	.491	2.028600
84	2.312800	.373	54520.	54521.	.491	2.063800
85	2.400000	.405	54888.	54877.	.499	2.300000
86	2.287200	.403	55835.	55843.	.501	2.273300
87	2.287000	.425	56289.	56287.	.492	2.273300
88	2.300600	.440	57261.	57267.	.485	2.300000
89	2.300600	.451	57571.	57579.	.482	2.300000
90	2.306300	.467	57726.	57724.	.488	2.300000
91	2.291600	.473	58692.	58699.	.492	2.262900
92	2.291300	.487	58996.	59002.	.514	2.262900
93	2.291300	.487	59155.	59152.	.505	2.262900
94	2.331600	.487	60166.	60172.	.492	2.254000
95	2.331600	.501	60485.	60482.	.503	2.254000
96	2.331600	.495	60753.	60748.	.494	2.254000
97	2.271100	.502	61591.	61594.	.497	2.124100
98	2.271100	.512	61897.	61909.	.494	2.124100
99	2.271100	.492	62130.	62124.	.518	2.124100
100	2.269300	.510	63060.	63063.	.479	2.132300
101	2.269300	.515	63507.	63501.	.486	2.132300

	----- GAC COLUMN ------			--- CONTROL COLUMN ----		
	FLOWRATE	CONC.	TIME	TIME	CONC.	FLOWRATE
102	2.277100	.417	64476.	64478.	.466	2.125500
103	2.277100	.520	64903.	64698.	.494	2.125500
104	2.234000	.525	65984.	65986.	.496	2.036500
105	2.234000	.542	66367.	66360.	.478	2.036500
106	2.130300	.543	67355.	67360.	.475	2.021000
107	2.130300	.546	67795.	67791.	.495	2.021000
108	2.183000	.544	68786.	68788.	.491	2.027400
109	2.183000	.566	69218.	69213.	.479	2.027400
110	2.183000	.556	70225.	70228.	.486	2.027400
111				70677.	.469	2.027400
112	2.336800	.558	71681.			
113				72117.	.474	2.020200
114	2.374400	.559	73125.	73125.	.491	2.088400
115	2.373100	.548	73573.	73564.	.469	2.080800
116	2.416000	.541	74596.	74567.	.459	2.160100
117	2.477800	.541	74820.	74820.	.456	2.222200
118	2.511600	.534	75009.	75000.	.033	2.186000
119	2.400000	.543	75328.	75323.	.022	2.226300
120	2.122900	.520	75991.	75994.	.013	2.225700
121	2.122900	.531	76420.	76416.	.009	2.225700
122	2.295000	.513	77443.	77446.	.007	2.129000
123	2.295000	.532	77878.	77872.	.007	2.129000
124	2.158600	.512	78878.	78879.	.004	2.299100
125	2.158600	.522	79332.	79334.	.004	2.299100
126	2.093500	.500	80312.	80326.	.003	2.349600
127	2.093500	.461	80924.	80928.	.003	2.349600
128	2.195400	.452	81745.	81753.	.002	2.253900
129	2.195400	.465	82304.	82304.	.002	2.253900
130	2.289800	.406	83205.	83210.	.001	2.237300
131	2.239100	.385	84716.	84722.	.002	2.200800
132	2.239100	.390	85134.	85132.	.001	2.200800
133	2.152500	.352	86089.	86085.	.001	2.239500
134	2.152500	.371	86518.	86516.	.001	2.239500
135	2.187000	.342	87504.	87511.	.001	2.239100
136	2.187000	.338	87927.	87926.	.001	2.239100
137	2.164800	.313	88945.	88953.	.001	2.229300
138	2.164800	.318	89330.	[illegible]	.000	2.229300
139	2.154400	.304	90384.	90393.	.000	2.224400
140	2.154400	.299	90845.	90653.	.000	2.224400
141	2.171000	.282	91843.	91852.	.000	2.291000
142	2.171000	.292	92270.	92270.	.001	2.291000
143	2.138000	.176	93300.	93304.	.000	2.330300
144	2.138000	.247	93706.	93708.	.000	2.330300
145	2.154000	.240	94751.	94792.	.000	2.313800
146	2.100500	.239	96217.	96220.	.000	2.314700
147	2.100500	.242	96651.	96655.	.000	2.314700
148	2.161500	.222	97643.	97653.	.000	2.279300
149	2.161500	.216	98104.	98105.	.000	2.279300
150	2.185000	.209	99085.	98168.	.000	2.261000
151	2.185000	.214	99670.	99664.	.000	2.261000
152	2.194500	.203	100531.	100538.	.000	2.236700

	GAC COLUMN			CONTROL COLUMN		
	FLOWRATE	CONC.	TIME	TIME	CONC.	FLOWRATE
153	2.506000	.192	101139.	101136.	.000	2.476200
154	2.413200	.160	101907.	101913.	.000	2.447700
155	2.230600	.166	102327.	102324.	.000	2.196500
156	2.248400	.123	103416.	103422.	0.000	2.112500
157	2.249000	.139	103840.	103835.	0.000	2.112500
158	2.249600	.124	104857.	104861.	.000	2.125300
159	2.245900	.131	105274.	105278.	0.000	2.125300
160	2.234200	.128	106222.	106225.	0.000	2.148900
161	2.234400	.129	106673.	106667.	0.000	2.148900
162	2.232000	.098	107676.	107681.	0.000	2.162400
163	2.226000	.125	108112.	108108.	0.000	2.162400
164	2.230600	.107	109136.	109139.	0.000	2.183900
165	2.301600	.126	109569.	109584.	.000	2.183900
166	2.294900	.117	110547.	110549.	0.000	2.150400
167				110996.	1.674	2.150400
168				111994.	1.782	2.144300
169				112422.	1.914	2.144300
170				113478.	1.711	2.207800
171	2.206100	.124	113900.	113698.	1.729	2.207800
172	2.269200	.131	114948.	114953.	1.809	2.170600
173	2.269400	.148	115378.	115369.	1.782	2.170600
174	2.236000	.154	116301.	116307.	1.850	2.176300
175	2.236800	.218	116757.	116752.	1.764	2.176300
176	2.244500	.573	117701.	117706.	1.842	2.160800
177	2.244500	.761	119192.	119198.	1.828	2.192100
178	2.244500	.753	119649.	119646.	1.779	2.192100
179	2.275000	.825	120636.	120622.	1.866	2.150800

11.3 TOC CONCENTRATIONS

	----- GAC COLUMN ------			--- CONTROL COLUMN ----		
	FLOWRATE (ML/MIN)	CONC. (MG/L)	TIME (MIN)	TIME (MIN)	CONC. (MG/L)	FLOWRATE (ML/MIN)
1	1.953600	.102	269.			
2				313.	4.590	2.033900
3	1.953600	.065	391.			
4	1.953600	.251	486.			
6	1.953600	.104	759.	766.	4.770	2.033900
5	1.953600	.127	1095.	1102.	4.730	2.033900
7	1.953600	.269	1410.			
8				1469.	4.830	2.033900
9				1751.	.241	2.033900
10	1.953600	.469	2140.	2147.	4.730	2.033900
11	1.945300	.583	3036.			
12	1.888300	.627	3532.	3540.	4.850	2.030800
13	1.888300	.568	4174.	4169.	4.730	2.030800
14	1.766400	.920	4768.	4768.	4.890	2.092600
15	1.766400	1.194	5620.	5636.	4.809	2.092600
16	1.812100	1.270	6439.	6445.	4.850	1.886400
17	1.812100	1.190	7123.	7148.	4.850	1.886400
18	1.812100	1.250	7192.			
19	1.812100	1.250	7210.			
20	1.726400	1.370	8324.			
21	1.726400	1.410	8562.			
22	1.726400	1.490	8762.			
23	1.726400	1.590	9273.	9280.	4.870	1.641400
24	1.726400	1.640	9710.	9722.	4.910	1.641400
25	1.748900	1.660	9988.			
26				10741.	4.880	1.722200
27	2.000100	2.130	12325.	12332.	4.870	2.107500
28	2.000100	2.270	12869.	12859.	4.830	2.107500
29	2.000100	2.330	13104.			
30	2.014900	2.390	13750.	13756.	4.850	2.127400
31	2.014900	2.450	14187.	14210.	4.870	2.127400
32	2.014900	2.500	14439.	14460.	4.850	2.127400
33	2.002800	2.560	15071.	15078.	4.890	2.123700
34	2.002800	2.600	15613.	15629.	4.830	2.123700
35	2.000900	2.720	16418.			
36	2.000900	2.760	16982.	17001.	4.850	2.111100
37	2.000900	2.780	17227.			
38	2.000900	2.840	17355.			
39	1.974300	2.820	17892.	17899.	4.670	2.081700
40	1.974300	2.800	18573.	18581.	4.870	2.081700
41	1.974300	2.840	18817.			
42	1.990600	2.930	19335.	19335.	4.680	2.052400
43	1.990600	2.930	20004.	20013.	4.690	2.052400
44	1.990600	2.930	20412.	20434.	4.870	2.052400
45	1.936700	2.930	20881.			
46	1.936700	2.910	21450.	21460.	4.880	2.081100
47	1.879500	2.970	22284.	22290.	4.830	2.028900
48	1.879500	3.030	22915.	22925.	4.830	2.028900
49	1.867300	3.050	23694.	23705.	4.770	2.056800
50	1.867300	3.030	24347.	24356.	4.830	2.056800

	FLOWRATE	CONC.	TIME	TIME	CONC.	FLOWRATE
51	1.747600	3.990	25606.	25607.	4.820	2.045400
52	1.747600	3.970	25737.	25738.	4.840	2.045400
53	1.694500	3.990	26593.	26594.	4.790	1.977300
54	1.694500	3.990	27199.	27200.	4.820	1.977300
55	1.731400	3.930	27969.	27969.	4.690	2.072500
56				28845.	4.890	2.072500
57	1.686600	3.910	29468.	29469.	4.850	2.034700
58	1.686600	3.870	30038.	30039.	4.850	2.034700
59	1.960000	3.950	30869.	30869.	4.850	2.047100
60	1.698000	3.910	31441.	31450.	4.830	2.047100
61	2.095000	3.950	32953.	32954.	4.850	1.983200
62	2.191100	3.990	33602.	33603.	4.850	2.075500
63	2.191100	3.950	34481.	34477.	4.810	2.075500
64	2.274100	3.930	35136.	35132.	4.830	2.024300
65	2.274100	3.900	35790.	35788.	4.790	2.024300
66	2.178600	3.820	36599.	36604.	4.830	2.046400
67	2.178600	3.840	37248.	37243.	4.830	2.046400
68	2.173800	3.860	38038.	38038.	4.830	2.039400
69	2.173800	3.870	38635.	38624.	4.830	2.039400
70	2.233500	3.710	39500.	39497.	4.810	1.983200
71	2.233500	3.720	40130.	40122.	4.790	1.983200
72	2.208200	3.700	41003.	41001.	4.830	2.003700
73	2.208200	3.700	41577.	41573.	4.810	2.003700
74	2.106000	3.640	42419.	42414.	4.870	1.968900
75				43026.	4.830	1.968900
76	2.119200	3.720	43843.	43843.	4.830	1.990500
77	2.119200	3.730	44532.	44529.	4.810	1.990500
78	2.095800	3.730	45269.	45266.	4.810	1.952900
79	2.095800	3.730	45916.			
80	2.028600	3.750	46675.	46674.	4.770	1.872100
81	2.028800	3.760	47302.	47298.	4.890	1.872100
82	2.006800	3.720	48125.	48123.	4.810	1.814300
83				48793.	4.890	1.814300
84	1.885700	3.720	49670.	49666.	4.710	1.695400
85	1.885700	3.790	50205.	50198.	4.830	1.695400
86	2.084500	3.810	50940.	50943.	4.830	2.052300
87	2.084500	3.890	51676.	51676.	4.810	2.052300
88	2.390000	3.950	53258.	53248.	4.810	2.025000
89	2.312900	3.870	53986.	53984.	4.810	2.063800
90				54650.	4.890	2.063800
91	2.287000	3.910	55357.	55360.	4.810	2.273300
92	2.287000	3.970	56019.	56019.	4.810	2.273300
93	2.306300	3.930	56773.	56776.	4.830	2.300000
94	2.306300	3.990	57416.			
95	2.291300	3.970	58206.	58209.	4.810	2.262900
96	2.291300	3.970	58820.	58829.	4.850	2.262900
97	2.331600	3.970	59655.	59657.	4.770	2.254000
98				60322.	4.810	2.254000
99	2.271100	3.950	61165.	61164.	4.790	2.124100
100	2.271100	3.990	61718.	61714.	4.790	2.124100
101	2.289300	3.950	62587.	62587.	4.790	2.132300

	GAC COLUMN			CONTROL COLUMN		
	FLOWRATE	CONC.	TIME	TIME	CONC.	FLOWRATE
102				63267.	4.790	2.132300
103	2.277100	3.970	63986.	63986.	4.810	2.125500
104	2.234000	4.030	65438.	65437.	4.830	2.036500
105	2.234000	4.030	66161.	66156.	4.790	2.036500
106	2.130300	3.970	66857.	66858.	4.850	2.021000
107	2.130300	4.010	67539.	67541.	4.830	2.021000
108	2.183000	4.030	68268.	68286.	4.870	2.027400
109	2.183000	4.030	68984.	68976.	4.870	2.027400
110	2.183000	4.050	69715.			
111	2.183000	4.030	70428.	70424.	4.830	2.027400
112	2.338600	4.090	71185.	71172.	4.890	2.020200
113				71866.	4.830	2.020200
114	2.374400	4.090	73297.	73291.	4.870	2.068400
115	2.195300	4.130	75176.	75166.	4.870	2.469600
116	2.225700	4.110	75852.	75858.	4.900	2.122900
117				76196.	4.900	2.122900
118	2.295000	4.160	76928.	76925.	4.930	2.129000
119	2.295000	4.160	77625.	77617.	4.890	2.129000
120	2.158600	4.220	78369.	78375.	4.870	2.299100
121	2.099500	4.160	79813.	79821.	4.890	2.349600
122	2.099500	4.140	80528.	80535.	4.850	2.349600
123	2.195400	4.140	81332.	81336.	4.890	2.253900
124				81951.	4.900	2.253900
125	2.289800	4.200	82752.	82758.	4.970	2.237300
126	2.289800	4.200	83398.	83396.	4.870	2.237300
127	2.239100	4.210	84247.	84247.	4.890	2.200800
128	2.239100	4.220	84897.	84893.	4.870	2.200800
129	2.152500	4.200	85600.	85606.	4.890	2.239500
130	2.187000	4.200	87006.	87010.	4.870	2.239100
131	2.164800	4.200	88428.	88438.	4.870	2.229500
132				89432.	4.980	2.229300
133	2.154400	4.100	89849.	89854.	4.790	2.224400
134	2.154400	1.400	90660.	90662.	.680	2.224400
135	2.154400	1.150	91064.	91065.	.067	2.224400
136	2.171000	.929	91447.	91452.	.054	2.291000
137	2.171000	.974	92029.			
138	2.138800	.705	93494.			
139	2.154000	.641	94237.	94237.	.040	2.313800
140	2.154000	.703	95070.			
141	2.100800	.556	95633.			
142	2.100800	.580	96352.	96363.	.056	2.314700
143	2.161500	.645	97142.			
144	2.161500	.482	97848.			
145	2.185300	.453	99378.	99374.	.056	2.261000
146	2.194500	.375	100087.	100091.	.034	2.236700
147	2.530300	5.810	100920.	101015.	9.210	2.439400
148	2.413100	6.950	101515.			
149	2.380500	6.970	102102.	102100.	9.410	2.317100
150	2.248400	7.250	102666.			
151	2.248400	7.350	103609.	103605.	9.260	2.112500
152	2.245900	7.930	104354.			

	----- GAC COLUMN ------			--- CONTROL COLUMN ----		
	FLOWRATE	CONC.	TIME	TIME	CONC.	FLOWRATE
153	2.245900	2.380	105116.	105115.	.619	2.125300
154	2.294200	1.153	105805.	105806.	.119	2.148900
155	2.294200	.939	106421.	106421.	.148	2.148900
156				107168.	.101	2.162400
157	2.282000	.619	107857.	107859.	.063	2.162400
158	2.301600	.627	108617.			
159	2.301600	.516	109404.			
160	2.294900	.421	110058.			
161	2.294900	.358	110746.			
162	2.267000	.432	111483.	111484.	0.000	2.144300
163	2.267000	.415	112186.	112183.	0.000	2.144300
164				112948.	0.000	2.207800
165	2.206100	.365	113690.	113695.	0.000	2.207800
166	2.269100	.340	114417.	114416.	0.000	2.170600
167	2.269100	.325	115155.	115153.	0.000	2.170600
168	2.236600	.260	115829.	115831.	0.000	2.176300
169	2.236600	.290	116496.	116494.	0.000	2.176300
170	2.244500	.255	117222.	117224.	0.000	2.160800
171	2.244500	.260	117887.	117863.	0.000	2.160800
172	2.244500	.230	119375.	119378.	0.000	2.192100
173	2.278000	.345	120127.	120127.	0.000	2.150800