THE EFFECT OF OZONATION ON THE BIODEGRADABILITY OF REFRACTORY ORGANIC SUBSTANCES IN WATER

BY

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ABSTRACT

Most sources of drinking water supply contain dilute concentrations of natural and synthetic organic substances which are not readily degraded by micro-organisms. Many of these compounds are known or suspected carcinogens, and/or may act as precursors for the formation of chlorinated hydrocarbons during the chlorination disinfection processes practiced in water treatment plants. The removal of these substances prior to chlorination is therefore desirable.

The objective of this study was to test the claim that the oxidation of these organic substances by ozone results in the formation of more readily biodegradable compounds. A 25 ℓ laboratory ozone contactor was designed and built to simulate the ozonation process in a typical water treatment plant. The apparatus was used to ozonate samples of surface water and dilute synthetic aqueous solutions at applied doses ranging from 20 mg/ℓ to 40 mg/ℓ. The biodegradability of ozonated and unozonated 10 ℓ samples was then evaluated in electrolytic respirometers, based on the changes in soluble Total Organic Carbon, Chemical Oxygen Demand, UV absorbance, and Biochemical Oxygen Uptake measurement.

The ozonation system successfully simulated full scale operating conditions, achieving greater than 90% ozone utilization.

Total Organic Carbon removal was described by a first order system with reaction rate constants ranging from 0.0041 min^{-1} to 0.023 min^{-1}.

Ozonation was found to improve the biodegradability of refractive organic substances in the three water sources examined. However the results show considerable variation depending on the particular source ozonated. Generally higher applied ozone doses improved biodegradability. Total Organic Carbon removal for the combined ozonation/ biodegradation process ranged from 10% to 70% depending on the specific ozone dose and water source.

For oxygen uptakes less than 2 mg/ℓ the respirometry equipment provided only qualitative evidence of bacterial activity. It is recommended that further studies should evaluate the use of an electrolytic respirometer which is independent of atmospheric pressure fluctuations.

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LIST OF ABBREVIATIONS

COD	Chemical Oxygen Demand
COD_P	Chemical Oxygen Demand after pretreatment but prior to ozonation and biodegradation
COD_O	Chemical Oxygen Demand after ozonation
COD_B	Chemical Oxygen Demand after biodegradation of the unozonated sample.
COD_{OB}	Chemical Oxygen Demand after ozonation and biodegradation.
ΔCOD_O	Change in Chemical Oxygen Demand for the ozonation process ($\Delta COD_O = COD_P - COD_O$)
ΔCOD_B	Change in Chemical Oxygen Demand due to biodegradation of the unozonated sample ($\Delta COD_B = COD_P - COD_B$)
ΔCOD_{OB}	Change in Chemical Oxygen Demand due to biodegradation of the ozonated sample ($\Delta COD_{OB} = COD_O - COD_{OB}$)
NH_3-N	Ammonia Nitrogen
NO_3-N	Nitrate Nitrogen
NO_2-N	Nitrite Nitrogen
OU	Oxygen Uptake
OU_B	Oxygen Uptake of the unozonated sample
OU_{OB}	Oxygen Uptake of the ozonated sample
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon

TOC_P	Total Organic Carbon after pretreatment but prior to ozonation and biodegradation
TOC_O	Total Organic Carbon after ozonation
TOC_B	Total Organic Carbon after biodegradation of the unozonated sample
TOC_{OB}	Total Organic Carbon after ozonation and biodegradation
ΔTOC_O	Change in Total Organic Carbon for the ozonation process ($\Delta TOC_O = TOC_R - TOC_O$)
ΔTOC_B	Change in Total Organic Carbon due to biodegradation of the unozonated sample ($\Delta TOC_B = TOC_P - TOC_B$)
ΔTOC_{OB}	Change in Total Organic Carbon due to biodegradation of the ozonated sample ($\Delta TOC_{OB} = TOC_O - TOC_{OB}$)
UV	Ultraviolet Absorbance
UV_P	Ultraviolet Absorbance of the pretreated sample
UV_O	Ultraviolet Absorbance after ozonation
UV_{OB}	Ultraviolet Absorbance after ozonation and biodegradation

SECTION 1

INTRODUCTION

The continued increase in the number of organic substances identified in drinking water supplies is of comparatively recent concern. Many of these compounds are known or suspected carcinogens to animals and humans, although their long term effects at the concentrations commonly found in water are not clearly understood. In particular the formation of various chlorinated hydrocarbons has been attributed to the chlorination processes practiced in most water treatment plants in the U.S. To ensure safe public water supplies the maximum removal of both natural and synthetic organics is therefore desirable.

A strong oxidant such as ozone may be used to reduce the Total Organic Carbon (TOC) concentration. For the case of ozonation, however, it is thought that the most significant TOC removal results from the subsequent biodegradation of the oxidized products so formed. Improvement in the biodegradability of the organics present provides a relatively low cost mechanism for organic removal, although, the comparatively high cost of ozone treatment favours the use of low oxidant doses. For this reason its application

is predominantly for drinking water rather than wastewater treatment.

The main objective of this study is to evaluate the effect of ozone on the biodegradability of refractory or persistent organics in surface waters typically used as a source for drinking water supply. Previous studies have not rigorously shown that ozonation improves the rate of biodegradation under these conditions.

To achieve this objective water samples must initially be ozonated under conditions analogous to full scale water treatment. The composition of the water sources chosen characterize those surface waters flowing through an industrially and agriculturally developed region, and a swampy area where a high concentration of natural organics may be expected. Because of the anticipated variability in sample composition for these sources a pure substrate prepared under laboratory conditions was also ozonated to highlight any observed trends.

SECTION 2

LITERATURE REVIEW

2.1 THE OCCURRENCE OF REFRACTORY ORGANICS IN FRESH WATER

A recent survey (EEC Report, 1977) showed that more than 700 organic chemicals have been identified in raw or treated water supplies. These comprise a mixture of naturally occurring and synthetic compounds, many of which are known or suspected carcinogens to animals and humans and hence pose a potential threat to public health and the environment.

The bio-persistent or refractory contaminants are of particular concern. The term refractory has been applied (Rosen, 1970) to those organics that, although not necessarily truly resistant to oxidation, persist excessively long to exert a characteristic pollutional effect in a receiving water. Although the long term impact of refractory substances, at the concentrations commonly found in these waters, is not completely understood, such properties as colour, taste, and odour have been found characteristic of waters containing bio-resistant compounds.

2.1.1 Natural Organics

The natural organics in water may be broadly classified into two groups:

(i) Non humic Substances

(ii) Humic Substances (HS)

The components of the humic group arise from the stepwise decomposition of various plant and animal products, of substances synthesized biologically and/or chemically from the breakdown products, and of microorganisms and their decomposing remains.

Non humic substances include carbohydrates, proteins, peptides, amino acids, fats, waxes, resins and other low molecular weight organic species. In general these compounds are relatively easily degraded by microorganisms present in surface waters and hence do not persist in the receiving water.

The major organic fraction in water consists of humic substances. These are amorphous, brown coloured, hydrophilic, acidic substances with molecular weights ranging from 10^2 to 10^5. As shown in Figure 2.1-1 humic substances are commonly classified into three main fractions based on their solubility in alkali and acid (Black and Christman, 1963; Schnitzer and Khan, 1972; Mallevialle, 1974). The humic acid (HA) fraction may be further subdivided into an alcohol extractable fraction classified as hymatomelanic acid, although it is not clear that this is truly a distinct fraction. Stevenson and Butler (1969), suggest that hymatomelanic acid is produced from HA's during fractionation.

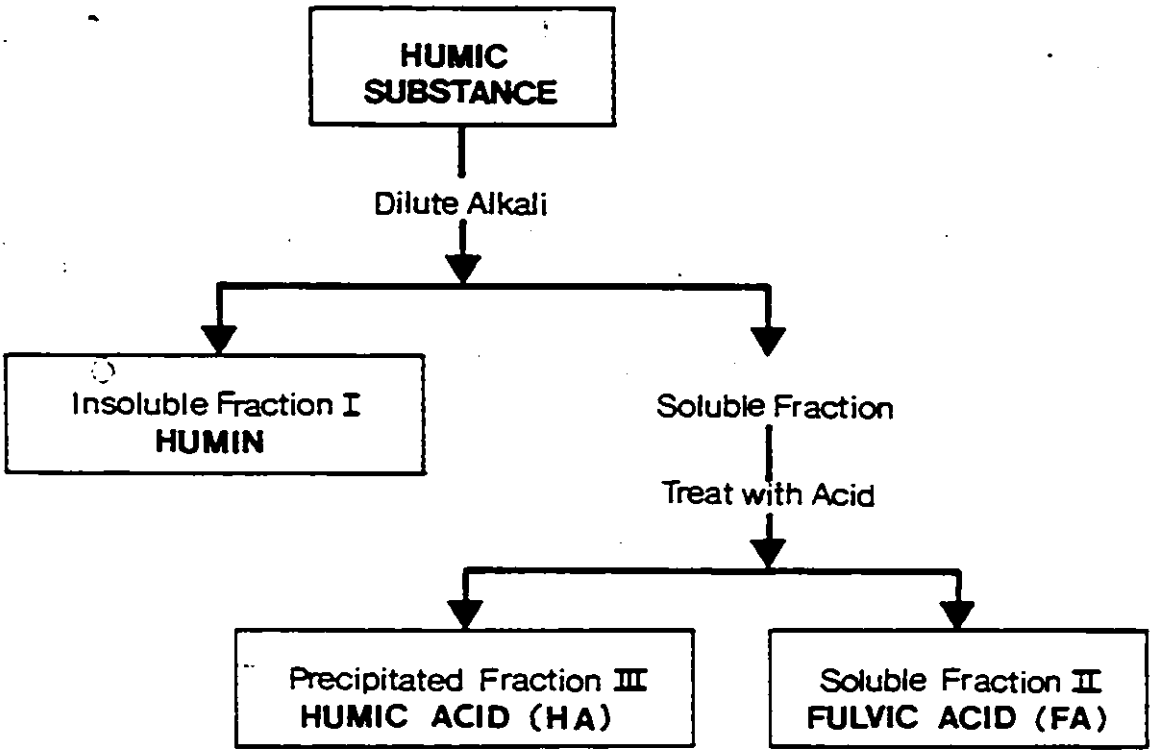


FIG. 2.1-1 FRACTIONATION OF HUMIC SUBSTANCES

Natural organic analyses by Lawrence (1978) of water from 27 Canadian rivers and lakes, indicated that fulvic acid (FA), humic acid, tannins, and lignins comprise the major portion of soluble organics in surface waters. In most instances the concentration of fulvic acid (1.9 - 23.0 mg/ℓ as Dissolved Organic Carbon) was reported to be a factor of 10 greater than that for humic acid and 3-30 times greater than the combined concentration of tannins and lignins. Similarly Black and Christman (1963) showed that the organic materials in coloured waters are predominantly of the fulvic acid type and that the relative amounts in each fraction were reasonably constant in the waters examined. However these characteristics may differ for various global locations. For instance Packham (1964) reports the following as a typical analysis of humic substances in British surface waters: Humic Acids (85%), Fulvic Acids (10%) Hymatomelanic Acid (4%).

In contrast to non humic substances, all humic fractions exhibit resistance to microbial degradation and hence are termed refractory. In Warburg respirometer studies by Helfgott, et al (1977), directed at establishing criteria for assessing the relative biodegradability of various compounds, Humic Acids in an aerobic environment seeded with domestic sewage organisms, were found to resist degradation almost totally over a 30-day incubation period.

Chemical Composition of Humic Substances

On an elemental basis humic substances are predominantly comprised of carbon and oxygen. Schnitzer and Khan (1972) summarized the composition of humic substances from a number of sources as follows:

ELEMENT	HA (%)	FA (%)
Carbon	50-60	40-50
Oxygen	30-35	44-50
Hydrogen	4- 6	3- 6
Sulphur	0- 2	0- 2

Acid hydrolysis of the humic substances indicates that 20-55% of the nitrogen is present as amino acid nitrogen. Khan and Sowden (1971, 1972) investigated the acid hydrolyzates of HA's, FA's, and humin fractions and showed aspartic acid and glycine were present in the largest amounts (12-14% each) with lesser quantities of alanine (7-11%) and glutamic acid (7-9%).

The major oxygen containing functional groups are carboxyls (-COOH), phenolic and alcoholic hydroxyls (-OH), carbonyls (-C=O) and methoxyls ($-OCH_3$). Of these most of the oxygen is present in carboxyl groups while phenolic -OH and carbonyls account for most of the remaining oxygen. (Black and Christman, 1963; Schnitzer and Khan, 1972).

Chemical Structure of Humic Substances

Structurally the humic fractions presented in Fig. 2.1-1 are thought to be similar, but with differences in molecular weight, ultimate analysis, and functional group content: the FA fraction having a lower molecular weight but a higher content of oxygen-containing functional groups per unit weight than HA's or the humin fraction.

Harworth (1971) concludes HA contains a complex aromatic core to which polysaccharides, proteins, simple phenols, and metals are chemically or physically attached. This may be shown diagramatically as in Fig. 2.1-2.

Furthermore, Ogner and Schnitzer (1971) and Khan and Schnitzer (1971) suggest FA is made up of phenolic and benzene carboxylic acids joined by hydrogen-bonds to form a polymeric structure of considerable stability. Based on analyses of isolated components Schnitzer (1971) has proposed the structure of FA shown in Fig. 2.1-3. It is postulated that the voids or peripheral groups characteristic of such a structure may adsorb or hold organic molecules such as alkanes, fatty acids, dialkyl and possibly carbohydrates, peptides, and pesticides, as well as inorganic compounds such as metal ions and oxides.

2.1.2 Synthetic Organics

In general the presence of synthetic, or man-made

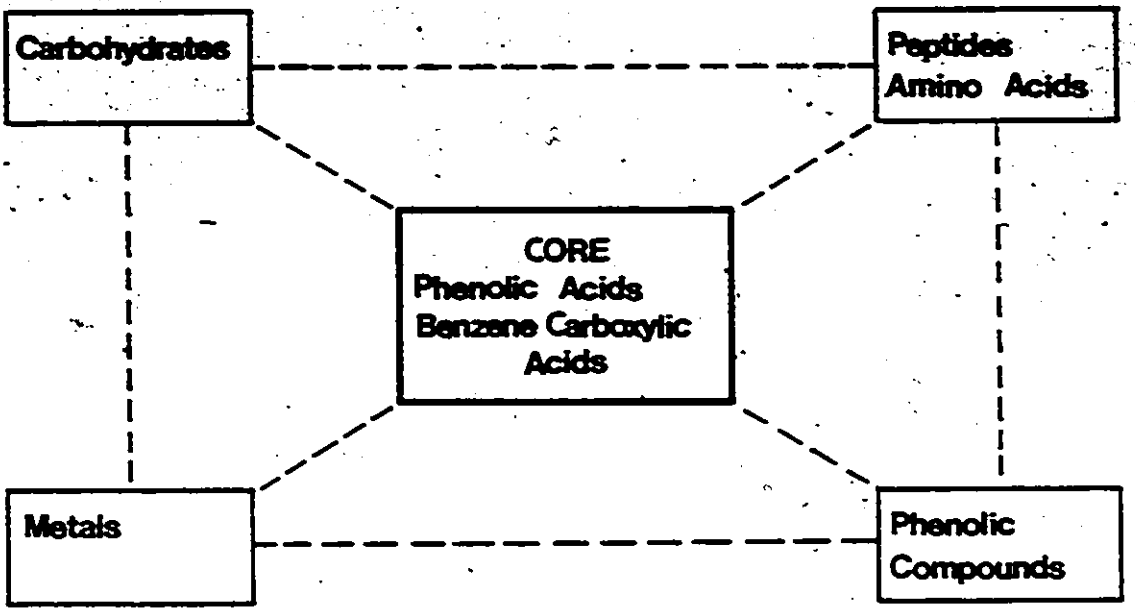


FIG.2.1-2 DIAGRAMATIC REPRESENTATION OF HUMIC ACIDS

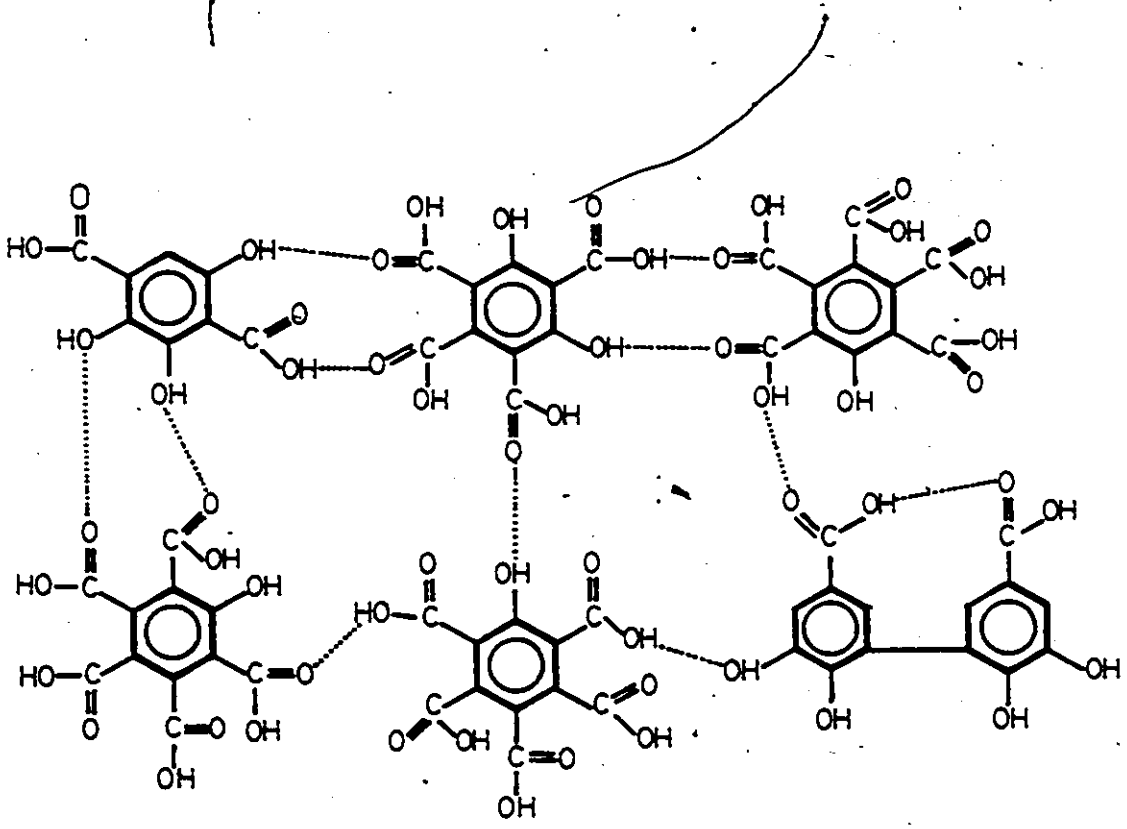


FIG.2.1-3 STRUCTURE OF FULVIC ACID PROPOSED BY SCHNITZER (1971)

organic chemicals in waters may be attributed to the extensive use of such compounds in industry and agriculture. Important sources of these contaminants include drainage from urban and agricultural land use, and the discharge of domestic and industrial wastewaters to receiving waters (Rosen, et al. 1972). Significant industries associated with such discharges include those related to the manufacture of textiles, pharmaceuticals, pulp and paper, polymers, and various other organic chemical processing. While a large number of these synthetic organics may be readily degraded biologically, the refractory and toxicity characteristics pertinent to many others has been widely acknowledged (A.D. Little Co., Inc., 1970). Among them are a variety of halogenated organics, aromatic and aliphatic hydrocarbons, and pesticides.

Recent studies by El-Dib and Aly (1976a, 1976b) revealed that phenylamide pesticide concentrations are constant in natural waters for more than four months. Similar persistence has been noted for the organo-chlorine insecticides such as benzene hexachloride (BHC), Dieldrin, Aldrin, and DDT (Croll, 1965 & 1968). These insecticides have been determined at concentrations ranging from 0.0-20.0 µg/ℓ in several U.S. rivers and English surface waters.

Fuchs and Kuhn (1975) report on organic pollutants, including a significant fraction of chlorinated organics in

water from the river Rhine. They noted a four fold increase in concentration over the period 1962-1975. Meijers and Van der Leer (1976), summarize their investigations on the same river in 1974 and concluded that the river Rhine is polluted by oil (0.1-1.0 mg/ℓ), a number of aromatics and aromatic bases (0.1-20.0 µg/ℓ) and a number of oxygenated substances.

The sources and occurrence of Polynuclear Aromatic Hydrocarbons (PAH) in water has been reviewed by Harrison, et al. (1975) and Borneff (1967). According to the latter 1-100 µg/ℓ of carcinogenic polynuclear aromatics can be detected in sewage, 0.01-0.10 µg/ℓ in surface water and 0.001-0.010 µg/ℓ in subsurface water. Although some PAH may be degraded, hydrocarbons of higher molecular weight than anthracene and phenanthrene showed no detectable degradation in studies by Malaney et al. (1967).

Humic substances, or other naturally occurring compounds may react with chlorine added to water for disinfection to produce chlorinated hydrocarbons (Rook, 1974; 1976) such as chloroform (Stevens, et al., 1976; Lawrence, 1977). In addition humic substances form stable water-soluble and water-insoluble salts and complexes with metal ions and hydrous oxides, and may act as carriers of synthetic organics such as pesticides and phthalates (Schnitzer and Khan, 1972; Buffles & Malleivalle, 1974). Several mechanisms have been postulated for the adsorption of such compounds by humics, the main ones being hydrogen bonding and ion exchange (Khan,

1972). Thus humic substances may increase the apparent solubility of synthetic organics and may in fact act to transport these organics through water treatment plants and into the body.

2.2 ABSORPTION AND DECOMPOSITION OF OZONE IN AQUEOUS SOLUTIONS

The absorption of ozone gas into aqueous solution is important in assessing process effectiveness. In addition to the means of gas dispersion used and the corresponding interfacial mass transfer resistance there are a number of other significant factors which affect the rate of absorption of ozone. Of primary importance is the rate of decomposition and reaction with organic solutes present in the water. Furthermore these reaction rates are influenced by the solution pH, temperature, pressure, and concentration of inorganic and organic solutes.

2.2.1 Decomposition of Ozone

The decomposition of ozone in the gaseous phase is a function of temperature and concentration (Benson and Axworthy, 1959). The rate of decomposition is slow under ambient conditions but greatly accelerated by heat. Typically a half-life of 20-100 hr. may be expected at room temperature in clean vessels of glass, stainless steel or other inert materials.

The mechanism and kinetics of ozone decomposition in aqueous solution are uncertain. Several complex decomposition mechanisms have been proposed along with varying conclusions concerning the order of the reaction relative

to ozone. However in aqueous solutions it is generally accepted that the decomposition of ozone to oxygen involves the formation and reaction of radicals of which the hydroxyl radical (OH) is one of the more important (Hoigné and Bader, 1975). All of the intermediate species formed are very reactive and possess short half-lives. By way of example, a number of the proposed mechanisms are presented in Table 2.2-1. Many investigators have studied the kinetics of ozone decomposition in water and in Table 2.2-2 the variability of their results concerning the reaction order relative to ozone is summarized. As can be observed from these results, the decomposition of ozone in water is complicated depending on the solution pH and possibly also on the oxygen content. In general it is recognized that ozone decomposition is catalysed by increasing pH or hydroxide ion concentration (Hewes and Davison, 1971). The experimental results of Kuo et al. (1976) indicate that the reaction rate constant increases with pH, and that the rate of increase is more rapid in alkaline solutions than in acidic solutions. By simplifying the overall reaction to: $2O_3 \longrightarrow 3O_2$ they concluded the rate of ozone decomposition may be best described by the equation:

$$\frac{d[O_3]}{dt} = - k_d[O_3]^{3/2}$$

Over the pH range 2.7 - 11.0 the reaction rate constant, k_d was found to increase by a factor in excess of 10^4. Similar

TABLE 2.2-1

MECHANISMS PROPOSED FOR THE DECOMPOSITION OF OZONE IN AQUEOUS SOLUTION

Reference	Weiss, 1935	Alder & Hill, 1950	Gorbenko-Germanov, Kozlova, 1977	McGrath and Norrish, 1958 (1)[e] Norrish and Wayne, 1965 (2) DeMore, 1973 (3) Thomas, 1965 (4) Czapski and Bielski, 1963 (5) Hochanansal, 1962 (6) Adams, et al., 1965 (7)
Experimental Media	Acidic-Basic	Acidic (Perchloric Acid)	Basic, (8M KOH, -50°C)	Water-Ozone vapour phase (1,2)
Mechanism	$O_3+OH^- \rightarrow O_2+HO_2$	$O_3+H_2O \rightarrow HO_3^- +OH^-$	$3O_3+2OH^- \rightarrow 2O_3^-+H_2O+2O_2$[a]	$O_3+H_2O \rightarrow O_2+2OH$[b] (1,2)
	$O_3+HO_2 \rightarrow 2O_2+OH$	$HO_3^+ +OH \rightleftharpoons 2HO_2$	$3O_3^-+H_2O \rightarrow O_2^-+3O_2+2OH^-$	$O_3+OH \rightarrow O_2+HO_2$ (2,3)
	$O_3+OH \rightarrow O_2+HO_2$	$O_3+HO_2 \rightarrow HO+2O_2$	$2O_2^-+H_2O \rightarrow HO_2^-+OH^-+O_2$	$O_3+HO_2 \rightarrow 2O_2+OH$
	$HO_2+OH \rightarrow O_3+H_2O$	$HO_2+HO \rightarrow H_2O+O_2$	$HO_2^- \rightarrow OH^- + \frac{1}{2}O_2$	$OH+OH \rightarrow H_2O_2$[c] (4)
	$HO_2+OH \rightarrow O_2+H_2O$			$OH+HO_2 \rightarrow H_2O+O_2$ (5)
				$OH+OH^- \rightarrow O^- +H_2O$ (6)
				$O^- + O_2 \rightarrow O_3^-$[d] (7)
				$HO_2+HO_2 \rightarrow H_2O_2+O_2$ (5)

[a] The authors suggest this step is probably initiated by: $O_3 + OH^- \rightarrow O_3^- + OH$

[b] At high pH Peleg (1976) suggests initiation state could be: $3O_3 + 2OH^- \rightarrow 2O_3^- + H_2O + 2O_2$

[c] Hydrogen peroxide reported by Thomas (1965) to further react: $OH + H_2O_2 \rightarrow HO_2 + H_2O$

[d] Felix, Gall and Dorfman, (1967) suggest the superoxide radical ion O_2^- may be a decomposition product of the ozonide ion O_3^-. As for Gorbenko-Germanov and Kozlova (1974).

[e] These references correspond to the mechanisms referred to below.

TABLE 2.2-2

SUMMARY OF THE KINETICS OF OZONE DECOMPOSITION IN WATER

Reference	pH Range	Temperature Range (°C)	Reaction Order with Respect to O_3
Rothmund & Burgstaller, 1913	2 ->4	0	2
Sennewald, 1933	5.3 ->8	0	2
Weiss, 1935	2 ->8	0	3/2
Alder & Hill, 1950	1 ->2.8	0 ->27	1
Stumm, 1954	7.6 ->10.4	1.2 ->19.8	1
Kilpatrick, et al., 1956	0 ->6.8	25	3/2
Kilpatrick, et al., 1956	13	25	2
Rankas, et al., 1962	5.4 ->8.5	5 ->25	3/2
Hewes & Davison, 1971	2 ->4	30 ->60	2
Hewes & Davison, 1971	6	10 ->50	3/2 ->2
Hewes & Davison, 1971	8	10 ->20	1
Czapski, et al., 1968	10 ->13	25	1
Rogozhkin, 1970	9.6 ->11.9	25	1
Merkulova, et al., 1971	.22 ->1.9	5 ->40	1 or 2
Kuo, et al., 1976	2.2 ->11.0	15 ->35	3/2
Rizzuti, et al., 1976	8.5 ->13.5	18 ->27	1
Shambaugh & Melnyk, 1976	9.0	20[a]	1

[a]Room temperature assumed.

results were obtained by Stumm (1958). Furthermore Hoigné and Bader (1976) have shown that the increasing rate of ozone decomposition at higher pH is matched by a corresponding increase in hydroxyl radical formation. The reaction of these radicals, and to a lesser extent ozone itself, with solutes present in the water may further accelerate or retard decomposition, depending upon the nature of the species present. It is postulated that the free radicals formed as a result of ozone decomposition act as carriers for further ozone decomposition. Thus if these radicals are scavenged by solutes, whose reaction products do not interfere with ozone molecules, then ozone decomposition is retarded. In some instances carbonate ions may react in this manner (Adams, et al., 1965). To illustrate the typical effect of solutes on the half-live of ozone in aqueous solution Table 2.2-3 is reproduced after Hoigné and Bader (1976). The rate of ozone decomposition was determined by measuring the decay of the U.V. absorbance at 258 nm. Although it is noted these values were obtained in solutions where the solutes also reacted appreciably, the reactive effects of pH and solute type are apparent.

Increased TOC removal has been reported (EPA Report, 1971; Hewes and Davison, 1972) when treating secondary wastewater with ozone and various metal salts. Hewes and Davison (1972) concluded that the catalytic effect was on the ozone

TABLE 2.2-3

HALF-LIVE VALUES FOR OZONE IN AQUEOUS SOLUTIONS AT 25°C[a]

Solutes (mg/ℓ)					Half Lives (Sec.) at Specified pH[b]			
benzene	Toluene	n-butanol	KCI	$NaHCO_3$	4	6	8	10
-	-	-	-	-	21,000	3,000	200	20
-	-	-	-	170		10,000	1,400	60
-	-	-	750	-		6,000	500	20
-	-	5	-	-	7,000	2,600	400	20
5	-	-	-	-	30	10	3	
5	-	5	-	-	2,000	400	20	
-	5	-	-	-	600	70	6	
-	5	-	-	170		90	10	
5	5	-	-	-	100	10	4	
5	5	5	-	-	600	100	10	
2.5	2.5	-	-	-	200	30	5	
2.5	2.5	-	750	-	1,000	50	5	

[a]Reproduced after Hoigné and Bader (1976)

[b]pH adjustment with 0.05 M sodium phosphate "buffers"

Initial Ozone Concentration: 12-14 mg/ℓ.

decomposition rate, thus increasing the formation of free radicals which further reacted with organic solutes.

In addition to the above effects the decomposition of ozone in aqueous solution is a function of temperature. The reaction rate constant (k_d) has been found to increase exponentially with temperature (Kuo, et al., 1976) at a given pH value, and the data correlated by the Arrhenuis equation:

$$k_d = b \exp(-E/RT)$$

where b = Frequency factor, which is a function of pH ($M^{-\frac{1}{2}} min^{-1}$)

E = Activation energy ($J. mol^{-1}$)

R = Universal gas constant ($JK^{-1}mol^{-1}$)

T = Temperature (K)

2.2.2 Absorption of Ozone in Water

Ozone Solubility

Ozone is more soluble in water than is oxygen, however because it is normally only available at low partial pressures, it is difficult to obtain a concentration of more than a few milligrams per litre under normal conditions of temperature and pressure. There is general agreement among the investigators that Henry's law is obeyed in the measurement of solubility data:

$$C_{os} = K_H P_{og}$$

where C_{os} is the saturation concentration of ozone in solution, K_H the Henry's law constant, and p_{og} the partial pressure of ozone in the gas. For the most part an ideal system may be assumed and thus the concentration of ozone in the gas C_{og}, in related directly to the concentration of ozone in the water C_{os}, each under the same conditions of temperature and pressure, (O'Donovan, D.C., 1965; Masschelein, W.J., 1971).

$$S_o = \frac{C_{os}}{C_{og}}$$

In Figure 2.2-1 the solubility or distribution coefficient is plotted as a function of temperature at one atmosphere.

However the achievable ozone concentration may be less than that predicted by Henry's law because depletion due to the decomposition reaction may dominate. This is especially the case under alkaline conditions and for water containing various organic solutes. This factor has important implications for ozone treatment processes in which the reaction rate is dependent on the soluble ozone concentration.

Mass Transfer

A number of theories have been proposed to describe interphase mass transfer. The two film theory, shown schematically in Fig. 2.2-2, in commonly applied to the absorption of ozone in water (Weber, 1972).

As ozone is only sparingly soluble at the low partial

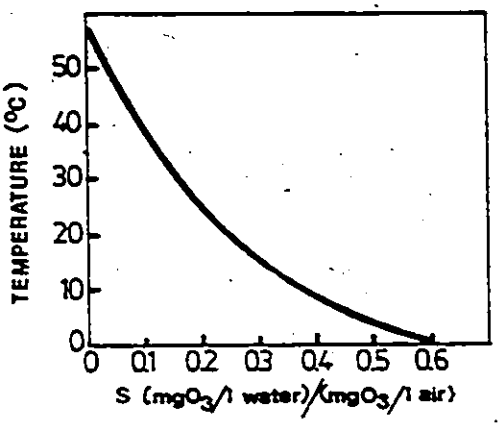


FIG.2.2-1 SOLUBILITY OF OZONE IN WATER AS A FUNCTION OF TEMPERATURE AT ONE ATMOSPHERE (O'Donovan, 1965)

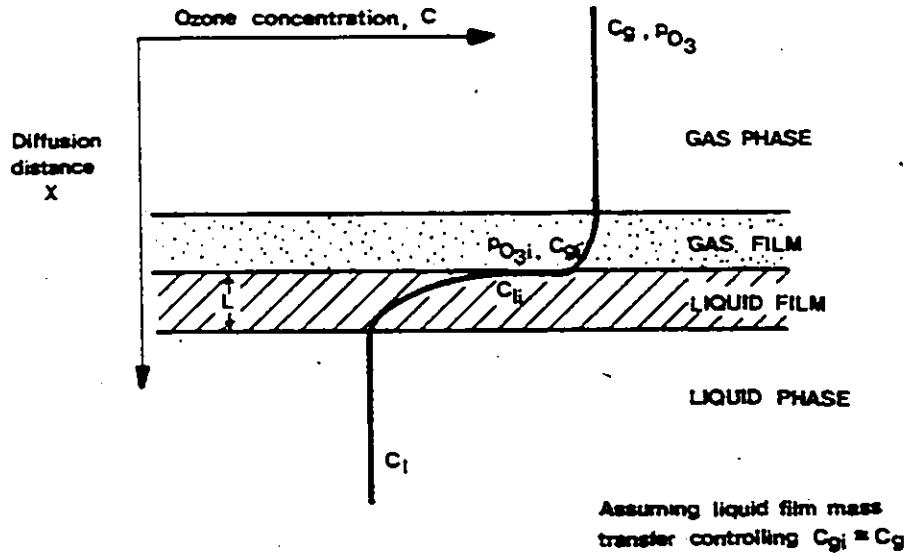


FIG.2.2-2 SCHEMATIC REPRESENTATION OF THE TWO FILM THEORY (Weber, 1972)

pressures after generation, the controlling resistance to overall mass transfer is considered to be in the liquid film. As a result the following expression may be considered:

$$N = K(C_{\ell i} - C_{\ell})$$

where N is the mass transfer rate per unit area (moles hr^{-1} cm^{-2}) $C_{\ell i}$ and C_{ℓ}, the ozone concentrations at the interface and in the bulk liquid respectively, and K the overall mass transfer coefficient (cm hr^{-1}). However the mass transfer kinetics of absorption are further complicated by the simultaneous reaction and decomposition of ozone in water (Heist, 1974). Many ozone kinetic studies are case specific because they combine the mass transfer properties and the reaction kinetics into one overall 'rate constant', rather than distinguishing between mass transfer rate and chemical kinetics. The literature published on the separate effects of these two basic phenomena is limited.

Mass Transfer with Ozone Decomposition and Chemical Reaction

In a number of cases the effects of mass transfer and decomposition on the absorption of ozone into distilled water has been determined. Shambaugh and Melnyk (1976) developed a model for a gas sparged batch ozone contactor based on first order decomposition of ozone in the bulk liquid but none in the liquid mass transfer film. Parameters found to affect the achievable solution ozone concentration

included the gas liquid interfacial area, (a) reactor pressure, (P) distilled water pH, the concentration of ozone in the gas, and the ratio of gas flow to reactor volume (G/V). Little change in the ozone concentration resulted from increasing a, P, G/V, beyond certain limits.

Kuo, et al.(1976) showed the kinetics of ozone decomposition in buffered distilled water to be 3/2 order with respect to ozone concentration and then used this information to model the absorption process by accounting for molecular diffusion and the decomposition reaction in the liquid film and bulk solution. Assuming one dimensional and steady state behaviour within the liquid film the mass transport accompanied by ozone decomposition is:

$$D \frac{d^2C}{dx^2} = k_d C^{3/2}$$

when $0 < x < L$ for $x = 0$, $C = C_{\ell i}$

$x = L$ $C = C_\ell(t)$

D molecular diffusivity of ozone in the liquid

C concentration of ozone;

$C_{\ell i}$ at the interface; C_ℓ in the bulk liquid

x distance

L film thickness

k_d reaction rate constant

The concentration of ozone in the bulk liquid is a function of time for the batch reactor under consideration. Then from

a mass balance the concentration of ozone in solution is given by:

$$V \frac{dC_\ell}{dt} = - AD \frac{dC}{dx}_{x = L} - Vk_d C_\ell^{3/2} , \quad x \geq L$$

V total volume of aqueous solution

A total interfacial area

t time, at $t = 0$ $C_\ell = 0$

These equations may be solved using a finite difference technique to obtain the concentration of ozone in solution for various conditions. A similar analysis involving a first order reaction in the liquid has been reviewed by Heist (1973).

The mass transfer coefficient, k has been determined in aqueous solution for a number of different contactor configurations (Hill and Spencer, 1973; Mallevialle, et al., 1975; Richards and Fleischman, 1975).

Few investigations have been directed at differentiating between the combined effects of ozone diffusivity, decomposition and reaction within the liquid film and bulk solution. In a study on the reaction of ozone with organics in municipal wastewater after secondary treatment Hewes and Davison (1971) observed that the reaction rate of ozone with the disolved organic compounds depended on the quantity of ozone decomposing rather than on the concentration of dissolved ozone. It is noted however that the rate of ozone decomposition depends on the ozone concentration. A two step

model has been proposed by Majumdar, et al. (1977) assuming mass transfer of ozone in the liquid film followed by a first order chemical reaction with organics in the liquid bulk. However no independent consideration has been given to ozone decomposition, the overall 'rate constant' for mass transfer presumably incorporating this effect.

2.3 OZONE CONTACTING SYSTEMS

A variety of systems have been used for the ozone-water contacting process, depending on the specific requirements of a particular application. However for each application the ozone contactor design considered should maximize the ozone mass transfer efficiency and minimize the net treatment cost. In this section the various types of gas liquid contactors are described, and the important parameters influencing the above criteria briefly reviewed.

2.3.1 Basis for Ozone Contactor Selection

There are at least three factors to be considered during the selection of an ozone-water contactor, as detailed below:

The Specific Process Application. Common fields of ozone gas-liquid application include: Municipal potable water or wastewater treatment, industrial water or wastewater treatment, or for use in industrial processes. Further definition of the particular application may be possible within each of these classifications (Stahl, 1973). For instance ozone treatment of potable water may be required for one or more of the following reasons:

- Odour, taste, or colour removal
- Iron or manganese precipitation

. Oxidation of refractory compounds

. Disinfection.

The Kinetics of Competitive Reactions. In general there are two major categories describing ozone reactions in solution.

(i) Rapid reactions limited by the rate of mass transfer of ozone into solution, e.g. bacteria, nitrites, phenols, unsaturated organics.

(ii) Reactions slower than the mass transfer rate and hence limited by the kinetics of the material to be ozonized, e.g. acetic acid, oxalic acid, ammonia, saturated aliphatic alcohols.

In designing an ozone contactor it is important to minimize the ozone dose for the specific purpose desired. For example bacterial disinfection requires rapid mass transfer. However for the oxidation of refractory compounds, or slow reacting species, maintaining a specific ozone concentration for a longer contact period may be more important than a high ozone transfer rate. In addition the effect of ozone decomposition in aqueous solution may be significant.

Mass Transfer Rates. Factors which affect the mass transfer of ozone in aqueous solution, and which themselves are affected by the design and operation of the contactor system include:

(i) The miscibility with water and the ozone demand of substances to be ozonated; both of which are a function of temperature and pH as discussed in Section 2.2. Typical ozone doses range between 1-10 mg/ℓ for the treatment of water for potable supply depending on the dissolved organics concentration and the purpose of treatment (Miller et al., 1978).

(ii) The type of carrier gas (air or oxygen) and corresponding ozone concentration. Increased mass transfer is favoured by higher ozone concentrations.

(iii) Method and time of contact. These parameters are further affected by the contactor configuration, mixing regime (cocurrent or countercurrent), and the gas dispersion system (diffuser or sparger).

(iv) Bubble size. Increasing interfacial area with decreasing bubble size favours mass transfer. However in practical terms the smallest bubble diameter generated from gas diffusers is approximately 2 mm (Sease, 1975). The bubble may further expand to 4-5 mm in diameter after passage through the fluid. As reported by Gomella (1972) the velocity of bubbles over

this range of diameters is 24-30 cm/sec.

(v) Total operating pressure of the system.

(vi) The presence of interfering substances, e.g. carbonates.

2.3.2 Ozone Generation

Ozone is produced when high voltage AC is imposed across a discharge gap in the presence of a gas containing oxygen. Various generation schemes affect the yield of ozone as reported by Rosen (1972). However the accepted basis for rating ozone generation is 1% concentration by weight in air. At higher concentrations successively less ozone is generated per kW/hr.

Dried air (Dewpoint -40 to -50^{o}C) is used as an oxygen source for ozone production in most potable water treatment applications. The ozone is optimally generated at pressures ranging from 0.7 to 0.8 bar.

2.3.3 Types of Gas-Liquid Contactors

Ozone gas-liquid contacting may be accomplished in a variety of systems as shown in Figure 2.3-1.

(i) Spray Towers

In spray towers liquid is dispersed in a gas creating a high degree of turbulence with good mixing characteristics. Although such units are relatively low in cost they are best employed for high solubility gases, where the number of

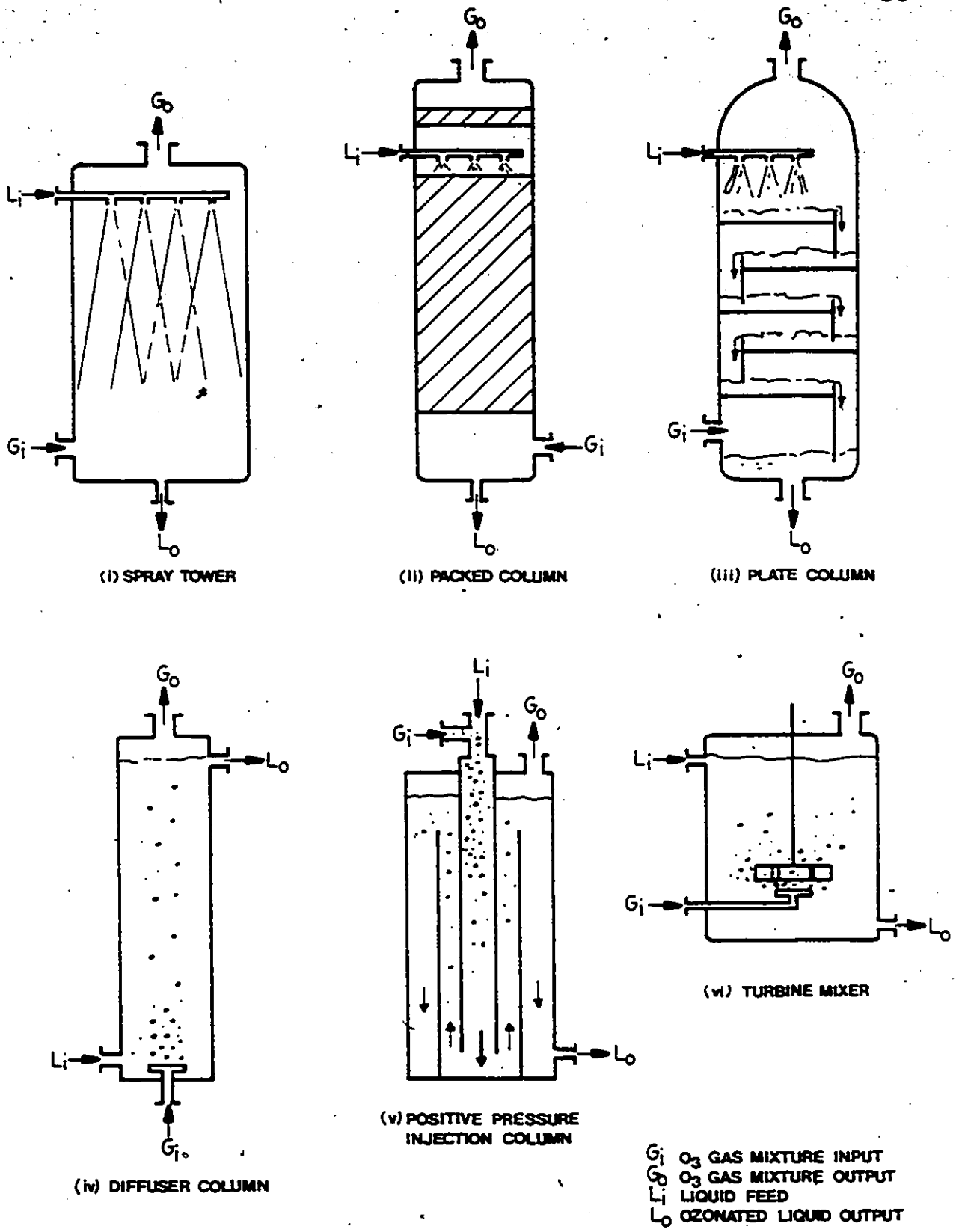


FIG. 2.3-1 OZONE GAS-LIQUID CONTACTORS

stages need not be large. As a result their use for ozonation is limited.

(ii) Packed Beds

In this instance the liquid is applied to the top of the column and flows through the packing, countercurrently contacting the ozone stream injected under pressure at the bottom. Advantages of such a system include a large surface area for mass transfer, low pressure drop, and a wide operating range of gas/liquid ratios allowing low and high ozone doses to be applied for rapid or slow reacting species. Problems of gas-liquid channeling and blocked packing may be encountered. Schwartz (1976) reports on a packed column ozone contacting system operating at the Sipplingen Berg Water Treatment Plant, Stuttgart, West Germany with an applied dose of 1 mg/ℓ and 97% utilization of ozone.

(iii) Bubble Plate and Sieve Plate Columns

Plate columns operate in a similar manner to packed beds and as such have many of the same advantages. In addition the gas stream is dispersed more uniformly through the liquid and the plate spacing arrangement generally facilitates cleaning.

(iv) Gas Bubble Dispersion Within a Liquid

The most common ozone contacting systems are based on some method for dispersing gas bubbles within a liquid. The gas may be introduced as bubbles of the desired size

or smaller, as in the case of porous diffusers (iv), or as massive bubbles which are disintegrated into the fluid by a turbine agitator (vi) or an injector (v). Numerous variations of these systems have been reported in the literature (Little and Spencer, 1973; Mallevialle, et al. 1975; Mignot, 1975; Masschelein, 1977; Scaccia and Rosen, 1977; Farooq, et al., 1978). A recent comparative evaluation of the performance of a diffuser column, a positive pressure injection column, and an agitated batch contactor led Scaccia (1977) to conclude, on the basis of theroetical and expermental results, that any type of commonly available contactor can be optimally designed to achieve the same degree of mass transfer, ozone disinfection or oxidation, and ozone utilization at approximately the same applied dose. The selection of a contactor then becomes one primarily based on economic considerations related to contact time, materials, and energy requirements.

2.3.4. Materials Selection and Safety Considerations

The equipment in full scale ozonation installations is of standard manufacture employing customary construction materials. For example no special requirements are necessary for concrete in contact with ozonated water. In general specific materials such as stainless steel are only required for surfaces in contact with ozone gas (Diaper, 1972).

However for precise experimental studies more inert and easily cleaned materials like glass, ceramics, teflon, and stainless steel should be used exclusively for ozonated air and air-water emulsions.

Although ozone is a toxic gas, for water treatment applications it is generated on demand at low pressures and concentrations. While the U.S. Public Health Service Safe working concentration is 0.1 ppm, a person may detect an ozoniferous odour at approximately 0.01 ppm and take the appropriate corrective action. Toxicity levels as a function of exposure time are shown in Figure 2.3-2.

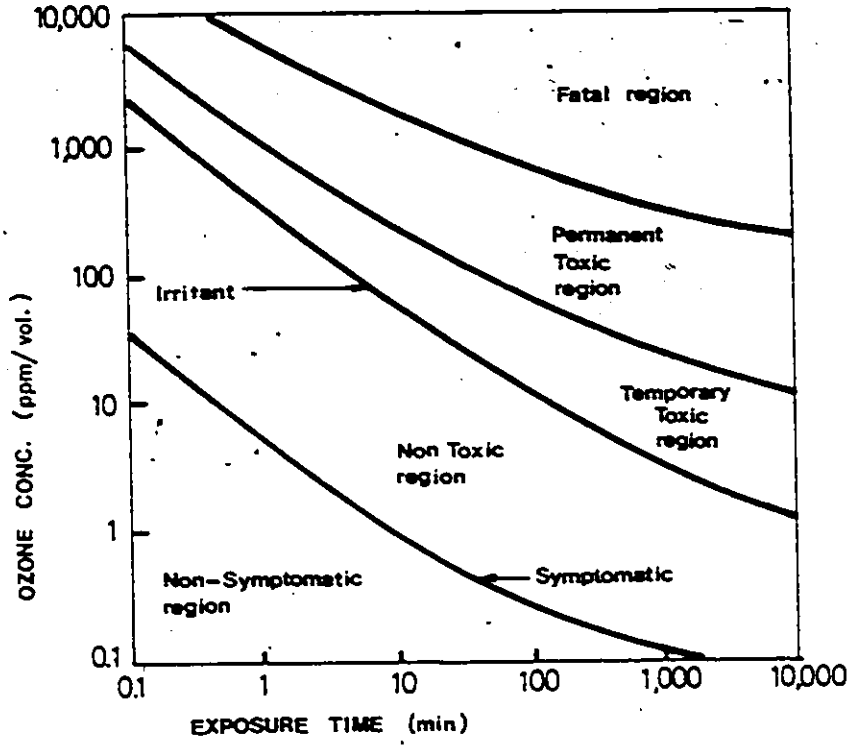


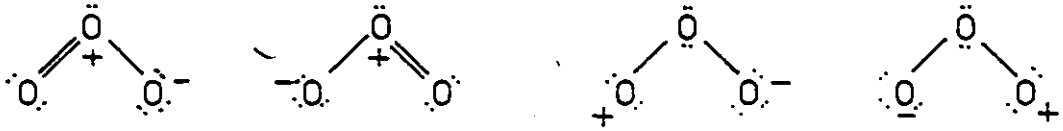
FIG.2.3-2 OZONE TOXICITY (Diaper, 1972)

2.4 REACTIONS OF OZONE WITH ORGANIC COMPOUNDS IN WATER

Ozone is a triatomic allotrope of oxygen which reacts with many organic compounds. The purpose of this section is to outline the mechanism, typical kinetics, and products formed when ozone reacts with the various organic functional groups of compounds commonly found in natural and some industrial waters.

2.4.1 Ozone Reactivity

The extreme reactivity of ozone is reflected in its oxidation potential (E_o = 2.07 V), which is the highest among the chemicals suitable for water treatment (Bollyky, 1977). Based on its microwave spectrum the ozone molecule is non-paramagnetic and can be described as a resonance hybrid of the following canonical forms (Bailey, 1972)



These structures suggest ozone should be able to react as an electrophile, nucleophile or as a 1,3-dipole.

2.4.2 Reaction Mechanisms

The basic mechanisms by which oxidants react with organic materials are:

(i) Addition; generally to compounds containing aliphatic unsaturation.

(ii) Substitution; whereby one atom or functional group is replaced by another

(iii) Oxidation; involving the introduction of oxygen, or an electron accepting atom or radical, into the organic molecule with or without degradation of the organic compound.

However the reaction of ozone with organic compounds in dilute aqueous solution, as found in water and wastewater, is further complicated by the hydroxyl ion catalyzed decomposition. Many of the reaction mechanisms proposed in the literature, for the ozonation of organic compounds, are based on experiments conducted at relatively high concentrations in non-aqueous solvents. These mechanisms, and the products formed, may not be operative when the same organic compound is ozonated in dilute aqueous solutions of less than 100 mg/ℓ (Hoigné and Bader, 1976; Maggiolo, 1976). Under these conditions the water may participate and be an initial part of the ozonated intermediate. Hoigné and Bader (1976) have shown that ozone may either react directly with substrates or, decompose prior to reaction to produce radicals such as the hydroxyl radical $^{\cdot}OH$ which may be more reactive than ozone itself. Baxendale (1964) gives a value for the oxidation potential of the hydroxyl radical as 2.8 V at $H^+ = 1.0$ M. The relative importance of each reaction is dependent on the solution pH, the

structure of the organic substrate, the reaction products formed, and any solutes that may enhance or retard ozone decomposition. These two pathways are shown schematically in Figure 2.4-1.

As the decomposition reaction is initiated by hydroxyl ions (OH^-) the free radical reaction mechanism is favoured by high pH. Conversely the direct oxidation mechanism predominates in the acidic region, or when solutes are present which react very rapidly with ozone molecules. In addition the preferred mechanism will determine the nature of the products formed.

Mechanism of Direct Reaction with Ozone (I)

Direct oxidation of an organic substrate is favoured by (Maggiolo, 1976);

(i) pH<8

(ii) No redox metal ions (Fe^{++}, Fe^{+++}, Mn^{++}, Mn^{+++})

(iii) Compounds with olefinic or acetylenic bonds, or those containing aromatic unsaturation that are reactive to electrophiles.

The pertinent reactions may be summarized as follows:

1. Reaction with Multiple Carbon-Carbon Bonds:

Ozone reacts, via 1-3 dipolar cyclo addition, with unsaturated bonds in organic compounds to form an ozonide intermediate which very rapidly reacts with water to form carboxylic acids and ketones. This mechanism for addition to a double bond

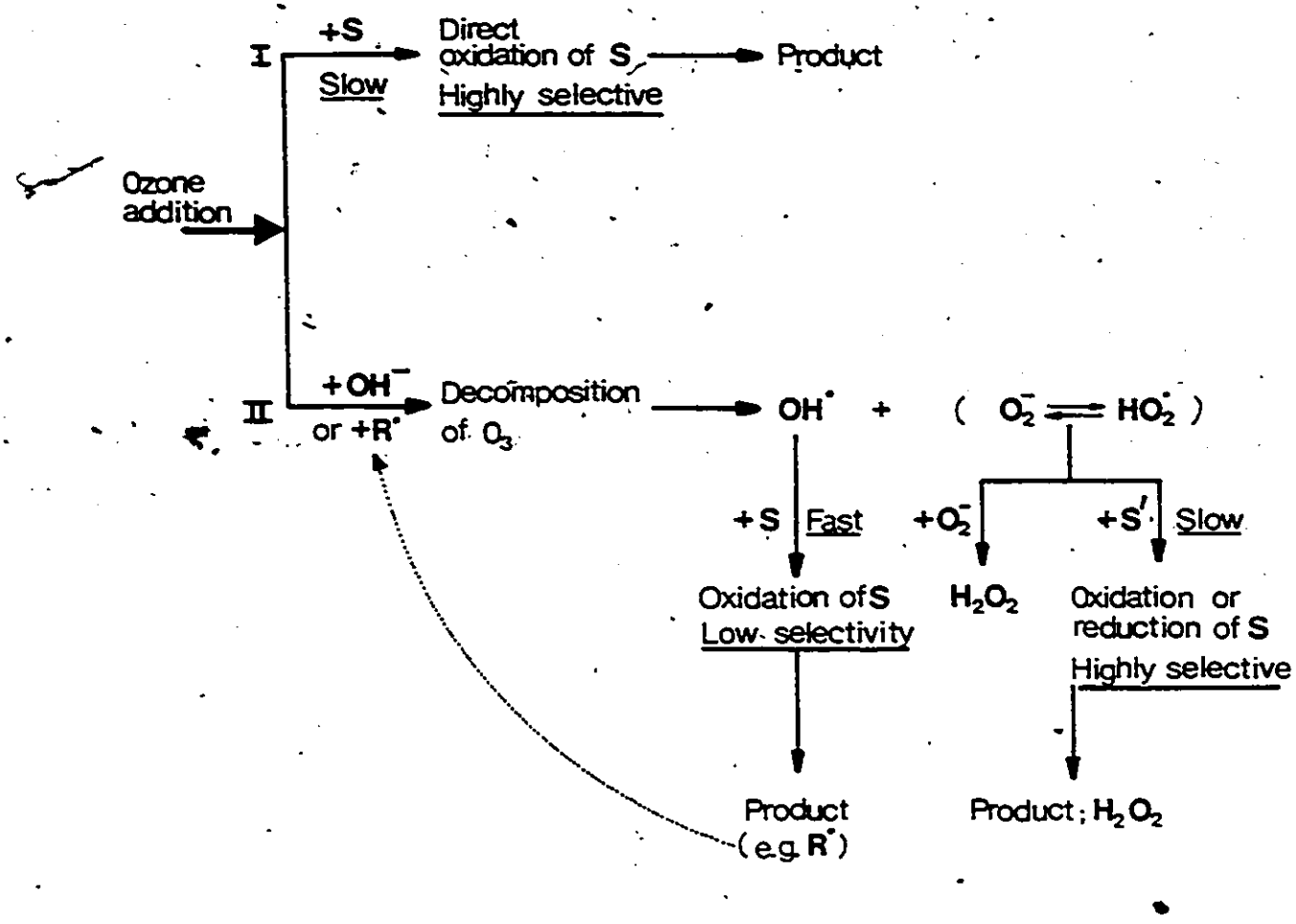


FIG 2.4-1 COMPETITIVE MECHANISMS FOR OZONE CONSUMPTION BY SUBSTRATES (S) IN AQUEOUS SOLUTION. S' refers to solute which retards ozone decomposition. (Hoigné, 1976)

in aqueous media is given in Figure 2.4-2. A detailed description is presented elsewhere (Bailey, 1972; Oehlschlaeger, 1976). Epoxide formation has been observed in solvent solutions after the ozonation of highly hindered double bonds, however in aqueous solution it is postulated these react with water to give either the glycol or its resulting aldehyde (Maggiolo, 1976).

2. Reaction with Aromatics: Ozone may react with the most reactive aromatic bonds by a 1-3 dipolar mechanism, or involve electrophilic attack on individual carbon atoms. With sufficient ozone the aromatic ring structure is fragmented. By way of example the mechanism for the ozonation of phenol in water is shown in Figure 2.4-3 (Eisenhauer, 1971; Bailey, 1972; Niki, et al., 1978).

3. Reaction with Nucleophiles: Nucleophiles commonly found in water include hydrogen sulphide mercaptans, amines and various other nitrogen, sulphur and phosphorus compounds including organophosphorus insecticides such as malathion. Ozone reacts as an electrophile with nucleophiles to form oxide products. In Figure 2.4-4 the reaction mechanism for the oxidation of a primary amine is described (Bailey, 1972).

It is noted however (Henbest and Stratford, 1964) that side-chain oxidation of amines may be the major reaction in aqueous media.

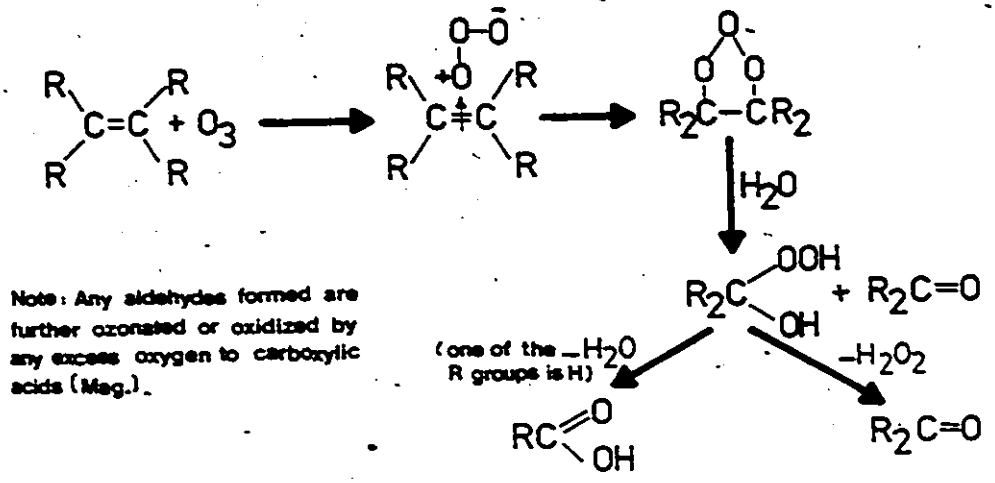


FIG 2.4-2 SIMPLIFIED MECHANISM OF OZONE-OLEFIN REACTIONS IN WATER (Maggiolo, 1978)

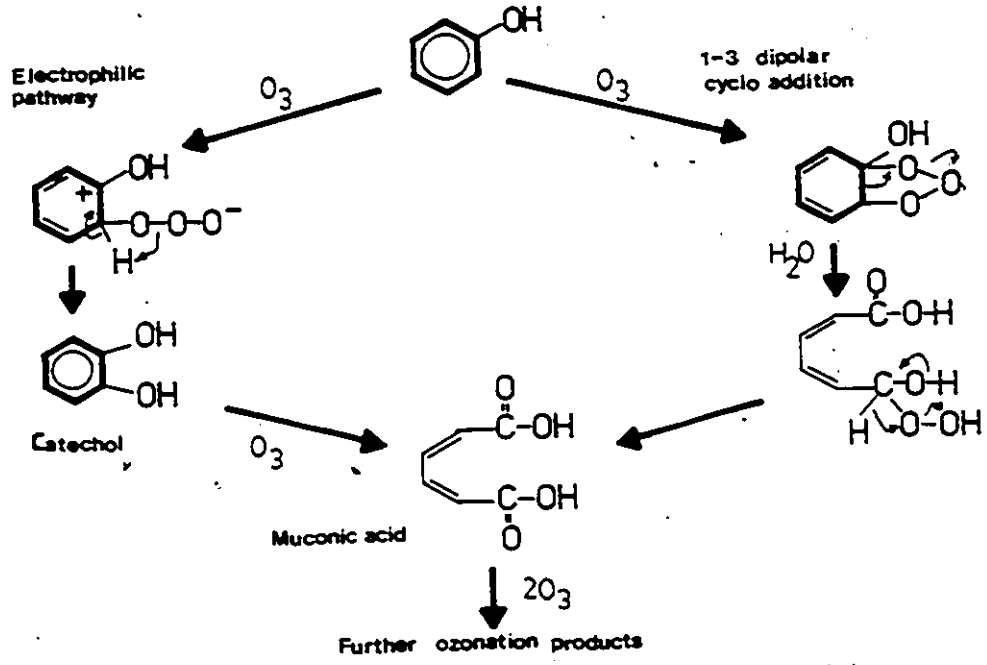


FIG 2.4-3 OZONATION OF PHENOL IN WATER (Bailey, 1972)

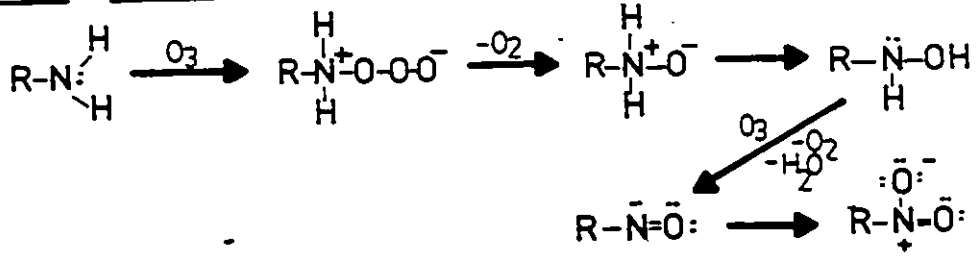
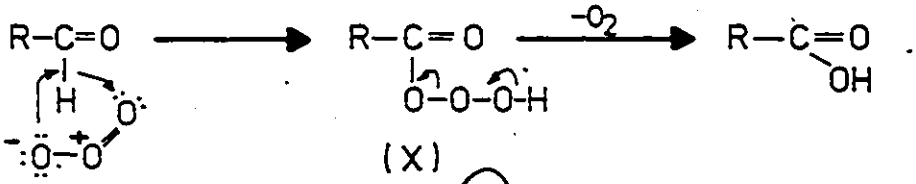


FIG 2.4-4 OZONATION OF A PRIMARY AMINE (Bailey, 1972)

4. Reaction with Aliphatic Alcohols, Aldehydes, and Hydrocarbons. When no reactive groups are present then ozone attack on carbon-hydrogen bonds is possible. The mechanism is thought to involve the formation of a hydrotrioxide intermediate (X)



(X)

Free Radical Mechanism (II)

This mechanism involves the formation and propagation of free radicals by reaction with the decomposition products of ozone in aqueous solution. Thus the reaction is favoured at pH's above 9 and in the presence of redox metal ions and oxygen. Hoigné and Bader (1975) have shown that above pH 8 ozone selectively decomposes to produce radicals (·OH and HO_2·) instead of reacting with the double bond of aromatic compounds. However with olefinic double bonds both direct and free radical mechanisms may operate simultaneously.

The free radical products of ozone decomposition in water react with organic compounds by addition to double bonds or by abstracting an active hydrogen to give organic free radical compounds, which may react in a number of ways to form hydroxy and carbonyl compounds (Maggiolo, 1976).

$$O_2 + RH \xrightarrow[\text{1. Sunlight; 2. Metal ions; 3. } O_3]{} R^{\bullet} + {}^{\bullet}OOH$$

$$R^{\bullet} + R'H \longrightarrow R'^{\bullet} + RH$$

$$R'^{\bullet} + O_2 \longrightarrow R'OO^{\bullet}$$

$$R'OO^{\bullet} + RH \longrightarrow R'OOH + R^{\bullet}$$

FIG2.4-5 PROPAGATION OF ORGANIC FREE RADICALS BY OXYGEN

Oxygen may also react to both oxidize aldehydes to acids and propogate organic free radicals. This mechanism is shown in Figure 2.4-5.

Further information on the effects of these hydroxylation reactions, including the type of products formed, may be obtained from data accumulated by radiation chemists and biologists (Anbar and Neta, 1967; Dorfman and Adams, 1973).

2.4.3 Reaction Kinetics

The kinetic constants pertaining to the ozonation of various organic compounds will be a function of the reaction mechanism followed. In some instances the direct reactions of molecular ozone may be important while in others the reaction rate will be determined by the reactions of $OH^{\bullet}$ radicals.

Direct Ozone Reaction Kinetics

A number of investigators (Hewes and Davison, 1972; Chain, et al., 1975; Hoigne and Bader, 1977) have shown 1st

order reaction rate characteristics with respect to ozone and solute (S) concentrations for the direct reaction of molecular ozone with organic compounds:

$$\frac{dS}{dt} = n \frac{dO_3}{dt} = -Ko_3 \cdot [O_3] \cdot [S]$$

n = yield of solute elimination based on ozone used per S eliminated

Ko_3 = reaction rate constant.

A limited number of reaction rate constant values have been reported in the literature for the direct reaction of ozone with organic solutes and many of these have been determined in non-aqueous solvents. Hoigné and Bader (1977) have calculated rate constants for a number of aromatic and aliphatic solutes in water by measuring the ozone depletion as a function of time or determining the relative elimination of two solutes. They concluded that ozone is a very selective oxidant and that the only solutes to be oxidized directly are those which contain a chemical bond of special reactivity towards ozone. The following observations are made:

(i) Ozone reacts rapidly with carbon-carbon double bonds (<1 sec) however chlorine substitution decreases its reactivity appreciably.

(ii) The reaction rate of benzene is relatively low but increases if benzene is substituted

with electron releasing substituents such as the alkyl group, methoxy and hydroxy groups. Conversely substituents which withdraw electrons from the ring such as nitro, halogens, and carbonyl groups, deactivate the ring towards ozone slowing down the reaction.

(iii) Aliphatic alcohols, aldehydes, and acids react very slowly with ozone. Formic acid, in its ionic form as formate ion, can be oxidized appreciably within minutes however oxalic acid does not react within a practical time period.

(iv) Amines react rapidly with ozone. For example the methylamines react about 10^3 times faster than ammonia.

Free Radical Reaction Kinetics

Reference to the kinetic rate constants for the reaction of OH· radicals with solutes may be obtained from studies in radiation chemistry and related fields. Hewes and Davison (1971, 1972) calculated pseudo first order constants for the removal of TOC from municipal wastewater after secondary treatment. They observed that the rate of removal is strongly affected by pH and temperature and is dependent on the rate of ozone decomposition and hence the formation of free radicals, rather than on the concentration of dissolved ozone. Together with studies by Huibers, et al.

(1969) it was concluded that the reaction between dissolved ozone and the organics is of negligible rate.

Similarly Augugliaro and Rizzuti (1978) identified two reaction mechanisms describing the pH dependence of ozone in aqueous phenol solution. The first mechanism, prevailing in acid solution, proposes first order kinetics in ozone, phenol and hydroxyl ion concentrations while the second, in basic solution, gives kinetics which are independent of the ozone concentration.

A mechanistic approach is described by Hoigné and Bader (1977) whereby OH^- radicals formed upon ozone decomposition may oxidize a solute or be consumed by scavengers present in the water. In natural water, carbonate and bicarbonate ions, and humic substances may act as scavengers to inhibit the ozonation of particular solutes. The rate of the sum of these reactions is determined by the rate of ozone decomposition in water. By comparison with the direct reaction of dissolved ozone with organic compounds the kinetics of the free radical reactions exhibit the following characteristics:

(i) Low selectivity

(ii) Rapid reaction with aromatic hydrocarbons, unsaturated compounds, aliphatic alcohols and formic acid.

(iii) The reaction of many refractory organics with ozone in water proceeds only by the free radical mechanism.

(iv) For both mechanisms, slow reaction of intermediate oxidation product such as acetic acid and oxalic acid. (Their rate data show that further oxidation to CO_2 would be minimal in practice, especially in the presence of more reactive solutes. This factor is supported by the many investigations reporting low Total Organic Carbon (TOC) removal rates by ozone treatment alone (Mallevialle, et al., 1976; Meijers, 1977).

2.4.4 Reaction Products

The reaction products of concern in this section are those pertaining to the ozonation of natural and synthetic refractory compounds found in water. However the majority of experimental studies dealing with organic oxidation products from ozonation have not been conducted under similar conditions to those practised in water or wastewater treatment plants. The progress of many reactions has been followed using relatively concentrated solutions in non-aqueous media. Limited work is reported on the practised ozone treatment of organic compounds in dilute aqueous solution, at low oxidant doses, short contact times, and with no pH control.

Humic Substances

By comparison with many organic compounds humic substances are relatively resistant to ozonation. A summary of some of the products identified after reaction with ozone is presented in Table 2.4-1. In general extended ozonation results in the formation of acetic, oxalic, formic and terephthalic acids, phenolic compounds and carbon dioxide.

Aromatic Compounds

In general aqueous solutions of aromatic compounds rapidly react with ozone to form an assortment of reaction products (Rice, 1977). For the reaction of a particular organic compound the relative distribution of these products at a specific time is a function of the extent of ozonation. In Figure 2.4-6 the types of products identified after ozonation are shown for a number of aromatic compounds.

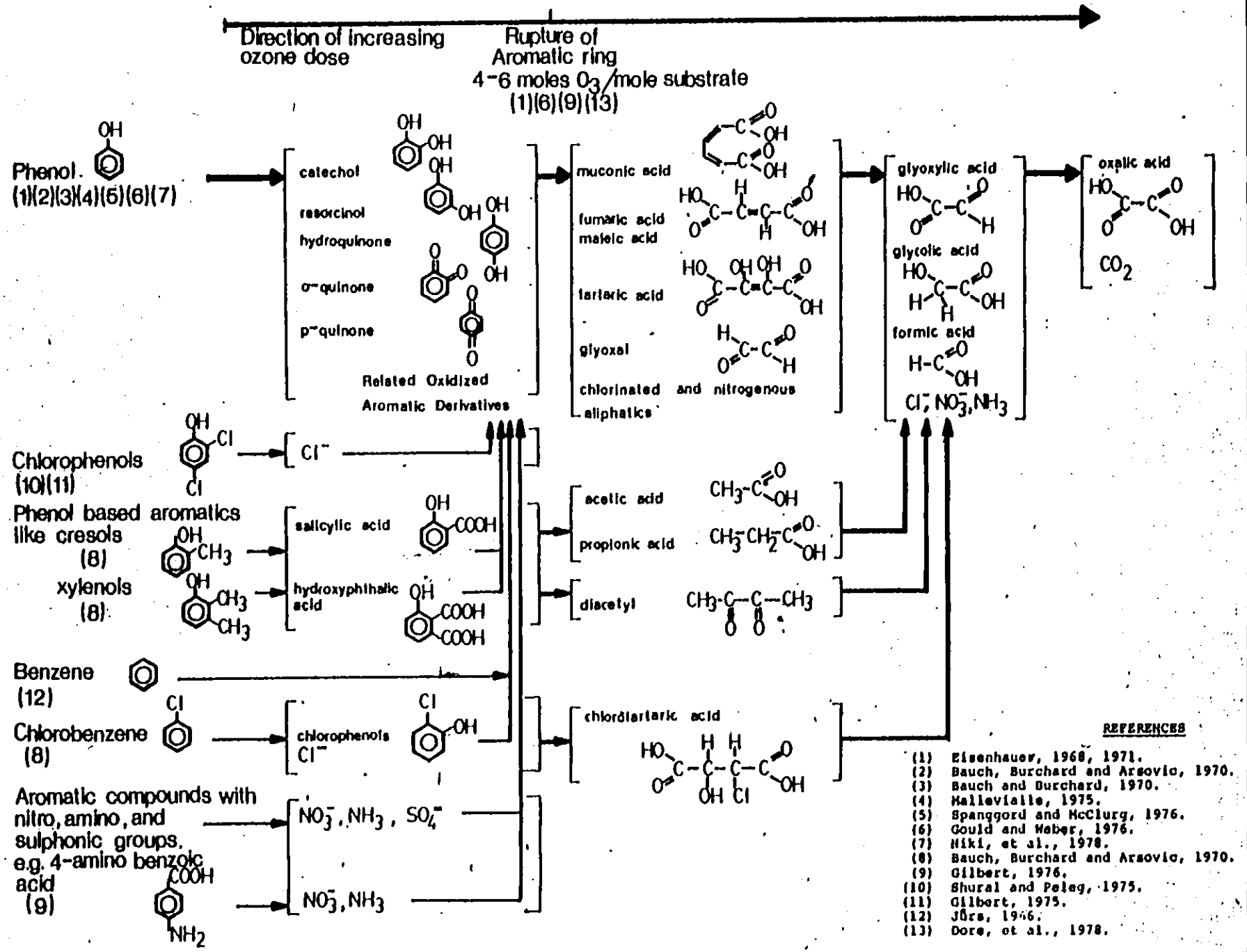
It is apparent that as ozonation proceeds the initial oxidation of these compounds is followed by degradation to low molecular weight carbonyl and acidic compounds. Experiments with dilute aqueous solutions of phenol, substituted phenols, and phenoxyacetic acids (Eisenhauer, 1968, 1971; Shuval and Peleg, 1975; Gould and Weber, 1976; Dore, et al, 1978) have shown 4-6 moles of ozone per mole of solute are required to open the aromatic ring. In addition nitro, amino, and sulphonic acid groups on aromatic rings are

TABLE 2.4-1

REACTION PRODUCTS AFTER OZONATION OF AQUEOUS SOLUTIONS CONTAINING HUMIC SUBSTANCES (HS)

Reference	Humic S Conc. (mg/ℓ)	Expt. Media and Reaction Volume	Gas Flow and Ozone Conc.	Contact Time or Applied O_3 Dose	Reaction Products Identified
Ahmed and Kinney, 1950	1000-2000	4% KOH 150 mls	15 ℓ/hr 56 mg/ℓ	0-48 hr.	Benzene carboxylic acids, acetic and oxalic acids, CO_2 carbonic and oxalic acids the major products - accounts for 65% of the remaining TOC, the rest being colourless, water soluble, ozone resistant acids.
Kinney and Friedman, 1952		alkaline aqueous			Oxalic acid, terephathalic acid, small amounts of acetic acid, and CO_2
Sherehenko and Taran, 1966	1000	aqueous		1.3 hr.	Oxalic, acetic, and formic acid, carbon dioxide
Buydens, 1970	river water	neutral aqueous		0.87-1.58 (mg/ℓ)	Higher suspended solids, phenol, and C.O.D. - possibly from fragmentation by decomposition of Fe and Mn from organic ligands
Mallevialle, 1975 et al., 1976	100-200	neutral aqueous 2.5 ℓ	66 ℓ/hr 24 mg/ℓ	0 - 2 hr.	Phenolic fragments, formic acid; Release of pesticide Lindane detected. Metal complexes liberated (Mn). Noted similar products formed by ozonation of salyicilic acid. 0.19 mg O_3/mg HS required for 95% colour reduction, 0.61 mg O_3/mg HS required for 95% polyhydroxyaromatic derivatives elimination 0,72 mg O_3/mg HS for 75% COD reduction 0.95 mg O_3/mg HS for 75% TOC reduction
Lawrence, 1979	1000, and 'high humic' raw water	neutral aqueous 500 ml	120 ℓ/hr.	1 hr. 475 mg/ℓ	Colour removal, lower MW compounds including branched, substituted, and simple dicarboxylic acids, low MW straight chain and branched acids, oxalic and acetic acids, phenoxy ketones and aromatic and nitrogen compounds.
Kuo, et al., 1976	oxalic acid 40-50 mg/ℓ	neutral aqueous	210 ℓ/hr. 25 mg/ℓ	0 - 2 hr.	Acetic acid oxidized to glyoxylic acid and then to oxalic acid slow oxidation of oxalic acids to CO_2

FIG.2.4-6 REACTION PRODUCTS IDENTIFIED AFTER OZONATING AQUEOUS SOLUTIONS OF AROMATIC COMPOUNDS



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(1) Eisenhauer, 1968, 1971.
(2) Bauch, Burchard and Arsovic, 1970.
(3) Bauch and Burchard, 1970.
(4) Malleviaile, 1975.
(5) Spanggord and McClurg, 1976.
(6) Gould and Weber, 1976.
(7) Niki, et al., 1978.
(8) Bauch, Burchard and Arsovic, 1970.
(9) Gilbert, 1976.
(10) Shural and Peleg, 1975.
(11) Gilbert, 1975.
(12) Jörs, 1966.
(13) Dore, et al., 1978.

split off by ozonation, although at rates below those observed for chlorine. Amino groups are converted to ammonia and nitrate ions.

It is proposed that in many instances the reaction products formed are more readily biodegraded than the original compound. However it is noted that the ozonation of some compounds (Cotruvo et al., 1977), such as the pesticides parathion and malathion (Richard and Brener, 1976) may result in the formation of more toxic compounds. Ozonation of parathion initially produces the more toxic material paraoxon. This is then degraded by continued ozonation. Robeck, et al., (1965) concluded, however, that the more usual drinking water treatment plant ozone dosages of 1-2 mg/ℓ would only oxidize parathion to paraoxon.

2.5 BIODEGRADATION

Biodegradation may be defined as the molecular degradation of an organic substance, usually in an aqueous medium, resulting from the complex actions of living organisms. In this section microbial activity and the factors influencing it are briefly described, along with the various methods of evaluating biodegradability.

2.5.1 Bacterial Growth Characteristics

Bacterial growth processes occur, predominantly in nutrified aqueous media, by mechanisms in which microorganisms convert dissolved organic carbon into carbon dioxide, water, and additional biomass:

$$\underset{\text{Substrate}}{\text{Organic}} + \text{Microorganisms} + O_2 \xrightarrow[\text{Aqueous System}]{\text{Nutrients}}$$

$$\underset{\text{Substrate}}{\text{Oxidized Organic}} + CO_2 + H_2O + \text{Microorganisms}$$

The process occurs in a stepwise fashion along specific metabolic pathways (Grady, 1978) in which organic molecules are successively further oxidized until carbon dioxide is produced. The microbial growth characteristics in a biodegradability test may be assessed as a function of time by monitoring the cumulative consumption of oxygen, the removal of soluble substrate, and the concentration of microorganisms. In Figure 2.5-1 these parameters are plotted

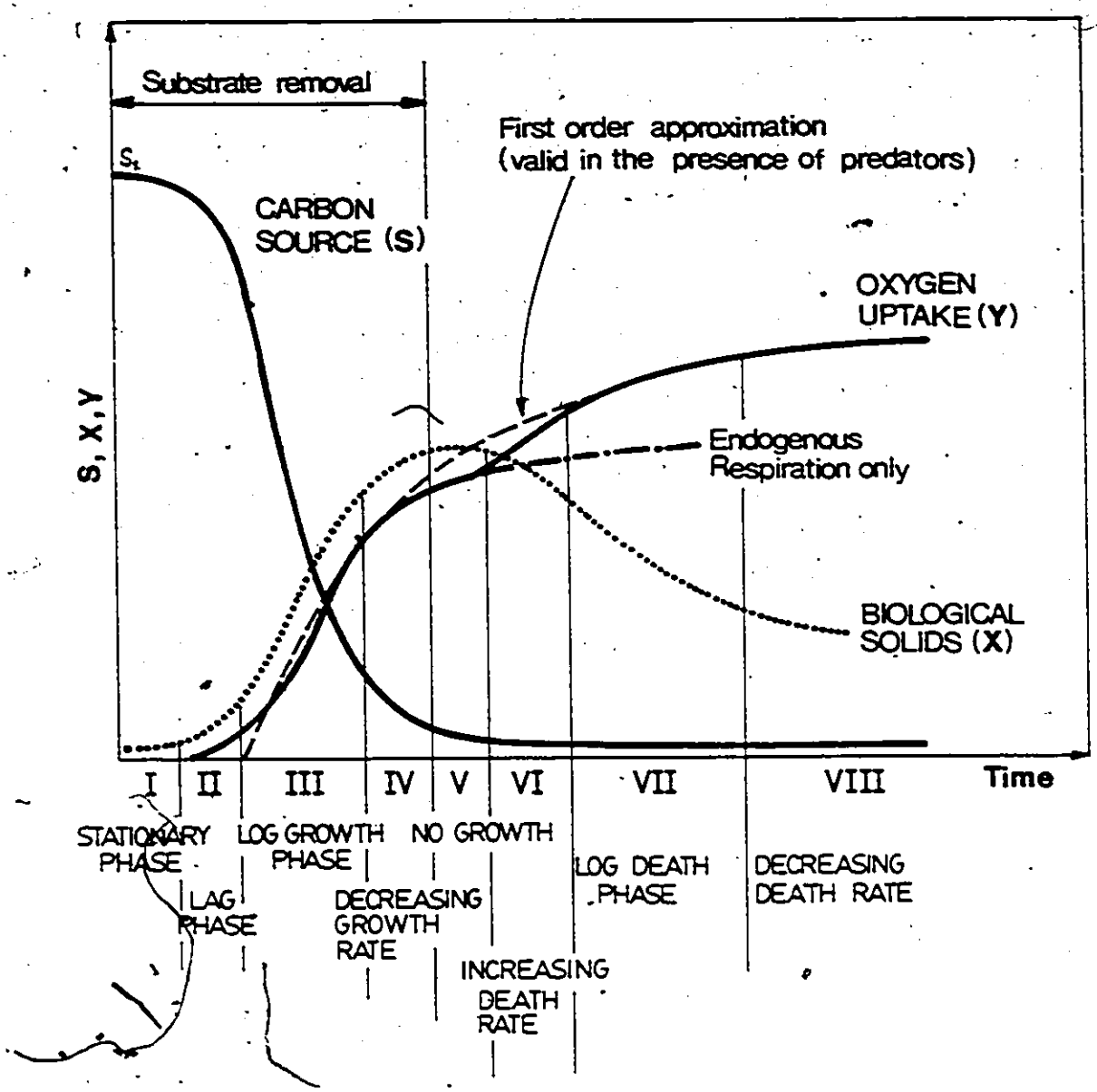


FIG. 2.5-1 TYPICAL GROWTH CURVE SHOWING SUBSTRATE CONCENTRATION (S), BIOLOGICAL SOLIDS CONC. (X), AND CUMULATIVE OXYGEN CONSUMPTION (Y).

for a system, initially with a substrate concentration S_1, and sufficient dissolved oxygen and inorganic nutrients. This figure shows that the point of complete substrate removal corresponds to the plateau in the oxygen uptake curve and the maximum concentration of biomass. This plateau, however, may be masked by a high fraction of bacterial predators such as protozoa or by a nutrient limited system (Busch, 1971). In this case the oxygen uptake curve more closely approximates a first order curve, with additional oxygen consumption from predators. Also shown in Figure 2.5-1 are the various phases of bacterial growth.

It is generally accepted that the kinetics of bacterial growth may be described by the empirical relationship proposed by Monod (1949):

$$\mu = \frac{\mu_m S}{K_s + S}$$

where μ Specific growth rate (hr^{-1})

μ_m Maximum specific growth rate (hr^{-1})

S Concentration of the growth limiting nutrient (mg/ℓ)

K_s Saturation constant (mg/ℓ)

The exertion of carbonaceous Biological Oxygen Demand (BOD) is commonly assumed to follow first order kinetics with the rate of oxygen utilization being proportional to the difference between the amount of oxygen used

(y) and the ultimate oxygen demand (L_o)

$$y = L_o(1 - \exp(-k_1 t))$$

k_1 first order rate constant

t time

Non carbonaceous matter may also exert an oxygen demand. For example the nitrogenous oxygen demand, arising from the oxidation of ammonia and organic nitrogen to nitrites and nitrates, may be significant in long term studies (Metcalf and Eddy, 1972; Young, 1973). At 20°C the reproductive rate of the nitrifying bacteria is very slow and normally approximately 10 days is required for them to reach significant numbers to exert a measurable oxygen demand. The influence of nitrification on tne oxygen uptake is shown in Figure 2.5-2 assuming first order carbonaceous BOD exertion.

2.5.2 Factors Influencing Microbial Activity

The microbial activity present in any test to determine the biodegradability of a particular compound is influenced by a number of biological and environmental conditions, the more important of which are briefly discussed below.

Inoculum Type and Concentration

The inoculum for a biodegradability test may be a pure or mixed culture of bacteria, which may also contain

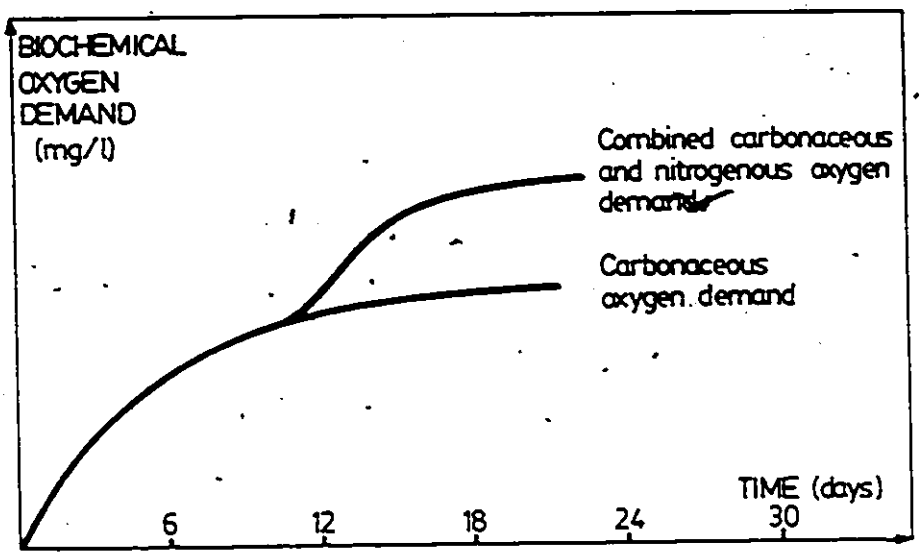


FIG.2.5-2 INFLUENCE OF NITRIFICATION ON THE BIOCHEMICAL OXYGEN DEMAND (Metcalf & Eddy, 1972)

protozoa. Furthermore the culture may or may not be acclimated to the substrate under consideration. The inoculum source selected is important in determining the micro-organism growth characteristics and thus the apparent biodegradability of the test material.

The affect of various pure and mixed culture inoculums on the rate and extent of biological oxidation of a particular compound, has been widely investigated (Montgomery, 1967). In a number of instances improved reproducibility has been claimed with the use of pure cultures (Ruchhoft, et al., 1939; Dillingham, et al., 1958), however larger oxygen uptakes are usually obtained with mixed cultures such as settled sewage (Lee and Oswald, 1959; James, 1964). Increased oxygen uptake in closed bottle tests has been partly attributed to the presence of predators, such as protozoa, in the inoculum. Reduced oxygen uptake and more reproducible results have been demonstrated using filtered sewage as a seed (Zehnpfennig and Nichols, 1953; Busch, 1958; Bhatla and Gaudy, 1965). Higher oxygen uptake may also be observed in long term studies when nitritying bacteria are present in the inoculum (Young, 1973).

If the bacterial inoculum has not been recently exposed to the test compound there will be a delay, or acclimation period, before biodegradation occurs. The duration of acclimation will depend on the degree of

adaptation required to establish new metabolic pathways for biodegradation. Greater changes of enzyme structure and specificity may be expected for compounds whose structure and properties differ appreciably from the earlier substrates of the inoculum. However once a suitable strain has developed biodegradation may be rapid. If the test compound is exposed to a large and varied source of bacterial inoculum the chances of rapid acclimation will also be increased. Furthermore the absence of other organic nutrients may accelerate acclimation, although strains capable of adapting may initially be lost owing to a lack of nutrients. The transfer to an artificial medium may also reduce the activity of the inoculum (Swisher, 1975).

It is commonly acknowledged that raising the concentration of inoculum increases the rate of oxidation but does not affect the plateau oxygen uptake (Heukelekian and Gellman, 1951; Wilson and Harrison, 1960; Rao and Gaudy,1966). A frozen seed source may be used to provide a uniform inoculum for a series of experiments, however extended lag periods using previously frozen sewage seed have been attributed to reduced bacterial concentrations in the inoculum (Lee and Oswald, 1954; Tyler and Hargrave, 1965). Similarly the diversity of species may be reduced after freezing.

Substrate

The resistance of a particular organic substrate to degradation may be related to its molecular structure

(Ludzack and Ettinger, 1960; Chambers, et al., 1963; Painter, 1974). The rate of biodegradation may be affected by the position, type, size, and number of groups incorporated on the structure. For example many aromatic compounds containing a nitro group are significantly resistant to degradation. High molecular weight materials and tertiary branched structures also exhibit reduced rates of degradability. The effect of substrate type is discussed in greater detail in Section 2.5.4. The effect of substrate concentration on the rate of oxidation has been studied with various conclusions being reported. In some cases increasing substrate concentration resulted in greater lag periods and increased rates of oxidation (Caldwell and Langelier, 1948; Dillingham, et al., 1958; Gaffney and Heukelekian, 1961) while Busch (1958), and Bhatla and Gaudy (1966), observed little effect on plateau values or on rates of oxidation over wide ranges of concentration. The increased rates of oxidation with higher substrate dilutions, found by others (Gellman and Heukelekian, 1953) using mixed substrates, may have resulted from the simultaneous dilution of toxic or inhibitory compounds.

Biodegradability tests in which the test compound is the sole source of organic carbon do not provide an environment for co-metabolism to occur (Horvath, 1972). Thus compounds that may be degraded by enzymes produced

by microorganisms feeding on other substrates present, may not biodegrade in single substrate experiments, or alternatively the rate of biodegradation may be slower. Similarly, higher concentrations of the substrate may be toxic to micro-organisms and thus exhibit inhibition, while degradation may be possible at lower concentrations.

Temperature

The rate of biochemical reaction is a function of temperature, as is the diffusion of substrate to micro-organisms. Various relationships proposed to describe this dependence are discussed by Busch (1971). Microbial activity generally increases with temperature, with the optimal temperature for bacteria commonly responsible for the biodegradation of organic compounds (e.g. Pseudomonas sp) being approximately 30°C. However most experiments are performed at controlled temperatures in the range 20°C to 25°C.

pH

The effect of pH on microbial activity is related to the deactivation of enzymes. The range of pH suitable for biodegradation is between 6 and 9. The test medium may require buffering should it be desired to maintain a constant pH.

Nutrients

A number of inorganic substances are considered as essential nutrients in bacterial metabolism:

(i) Dissolved Oxygen: Aerobic microbial systems require oxygen for growth. The theoretical or stoichiometric oxygen requirement is that necessary to oxidize all the carbon present to carbon dioxide. In practice, Kalinske (1971) concluded from a review of previous work that dissolved oxygen concentrations from 0.5 to 35 mg/ℓ do not affect respiration rates as long as the bacteria remain dispersed. For biodegradability tests involving reduced turbulence higher minimum concentrations may be required to provide the necessary gradient for mass transfer.

(ii) Carbon Dioxide: Carbon dioxide or bicarbonate is assimilated by some heterotrophic bacteria for the synthesis of intermediates required for growth (Werkman, 1951). Gaffney (1965) observed the effect of carbon dioxide in the oxidation of glucose and sewage by mixed microbial cultures. Subsequent to inoculation glucose (1000 mg/ℓ) was rapidly depleted in a carbon dioxide enriched atmosphere, however in a carbon dioxide-free air system a lag period of two days was reported. Further experiments in Warburg respirometers indicated the presence of carbon dioxide (CO_2) enhanced the initial oxygen uptake rate. A 1 to 2% CO_2 atmosphere was maintained in the Warburg vessels by

using diethanolamine solution, as described by Pardee (1949) and Krebs (1951). However Krebs (1951) notes that diethanolamine solutions absorb measurable quantities of oxygen and controls are required to correct for this.

In electrolytic respirometry tests lasting a few hours, with relatively high concentrations of both the substrate and sewage inoculum, Montgomery, et al. (1971) observed no significant difference between BOD curves obtained with and without alkali absorption of carbon dioxide. It was concluded carbon dioxide deficiency under these conditions was unlikely to occur, however in 'control' experiments, with no added substrate, it was thought advisable to omit the potassium hydroxide solution. The resulting error is a function of the gas to liquid ratio, but for their system was calculated to be less than 5.6%.

Slower substrate utilization and oxygen uptake, as a result of reduced bacterial activity, have been reported in respirometric studies by Tebbutt and Berkun (1976) and Ilic (1977) when using potassium hydroxide for carbon dioxide absorption. Although the degree of substrate oxidation may be similar to that under atmospheric conditions the bacterial growth rate, and hence oxygen uptake rate, appears to be reduced for the case of CO_2 absorption. In some cases however, the requirement for carbon dioxide may be replaced by compounds yielding carbon dioxide. These

are discussed by Werkman (1951); included are glutamic acid and four carbon chain dicarboxylic acids.

Nitrogen and Phosphorus: Quantities of these elements are required in proportion to the net cell growth in a particular system. Based on the work of Sawyers (1956) and Schaezler, et al. (1969) using glucose as a substrate. BOD_5:N and BOD_5:P ratios of 13:1 and 120:1 respectively were found to be sufficient for the maximum synthesis of cells. The actual requirements for a specific situation may vary according to the degree of treatment and the form in which the nutrients are applied (Helmers, et al., 1952). For example in the BOD test Lewis and Busch (1965) showed that nitrogen should be added as ammonia and not as nitrate.

Trace Nutrients: A variety of elements such as Potassium, Magnesium, Iron, and Calcium may be required for sustained microbial activity (Grady, 1978). In most natural systems the concentrations present are sufficient for growth.

Other Factors

(i) In long term biodegradability studies light should be excluded as the growth and photosynthesis of algae may interfer with oxygen uptake (Dawson and Jenkins, 1949).

(ii) Nitrification may be effectively suppressed in long term respirometric tests using

2 mg/ℓ concentrations of 2-chloro-6 (trichloromethy))pyridine (TCMP), however it is slowly hydrolyzed to 6-chloropicolinic acid, which although not toxic may be biodegradable (Young, 1973).

(iii) In respirometric tests sufficient agitation should be provided to keep the cells in suspension and manitain desired concentrations of dissolved oxygen (Lamb, et al., 1964: Young and Baumann, 1976).

2.5.3 Methods of Evaluating Biodegradability

When an organic compound is exposed to bacteria under specific test conditions its biodegradability may be assessed by various analytical methods monitoning the compounds removal or the metabolic activity of the bacteria. The test method selected should simulate the environment to which the results are to be related. However this is seldom possible, meaning any results obtained must be carefully interpreted.

Analytical Techniques for Evaluating Biodegradability

(i) Oxygen Uptake and Carbon Dioxide Evolution

As aerobic microbial activity involves the consumption of oxygen and the evolution of carbon dioxide these two parameters may be used to assess the biodegradation

of organic compounds. Oxygen levels may be measured by the Winkler method (Standard Methods, 1975) manometric methods, or the oxygen electrode, and carbon dioxide has been determined by absorption in barium hydroxide (Sturm, 1973).

The extent of biodegradation may depend on the type of test condition. In addition the method involves a simultaneously run control (containing no test compound) to correct for endogenous respiration by the bacteria. The validity of this correction is based on the assumption that the endogenous respiration rate is unaffected by the test compound. Thus the results are subject to a certain degree of uncertainty. The formation of new cells also means a portion of the carbon present is not released as carbon dioxide. In this regard a compound may be considered substantially biodegraded if more than 50% of the theoretical oxygen uptake is measured by the time the plateau in the oxygen demand curve (see Figure 2.5-1) is reached. Normally, in five days most of the cells synthesized are also degraded and the oxygen demand for degradable substances is greater than 70% of the theoretical value.

(ii). Dissolved Organic Carbon (DOC)

The determination of dissolved organic carbon has been commonly applied to biodegradability studies in which

the test compound is the sole source of carbon. Biodegradation is indicated by significant losses of dissolved organic carbon. Again a control with no substrate is required for correcting the organic carbon added with the inoculum.

(iii) Chemical Oxygen Demand (COD)

This technique may be used in conjunction with DOC information to estimate partial degradation of the test compound. In this instance the substrate may be partially oxidized without the loss of carbon from solution or less carbon than accounts for the change in COD.

(iv) Specific Chemical Analysis

A specific analytical method may be used to follow the disappearance of a test compound. This method is often employed to determine the biodegradability of surfactants, and is also applicable in biodegradation tests where other carbon sources are present (Fischer, et al., 1975). However sensitivity may be limited in mixed substrates due to analytical interferences, and information is not provided on the concentration of intermediates or residues.

(v) Other Techniques

A number of other techniques have been used, although less commonly, to evaluate biodegradability. These include the degradation of radioactively labelled

compounds (Kirsch and Etzel, 1973), monitoring the biomass concentration, and determining the biomass dehydrogenase enzyme activity (Thompson, et al., 1960).

Test Methods

The test methods available for determining the biodegradability of organic compounds may be broadly classified as being either Die-away tests or Activated Sludge type tests. Die-away tests are further grouped into those in which the test compound is the sole source of carbon and others where additional organic nutrients are present. A number of methods within these categories have been summarized by Ludzack and Ettinger (1960), and Gilbert and Watson (1977).

Activated sludge tests, designed to simulate sewage treatment, are characterized by a high biomass concentration and the continuous addition of a mixed organic substrate. These methods are of limited value for assessing the biodegradability of organics at the low concentrations present in surface waters, unless a specific chemical analysis technique is being considered. Similarly, if the biodegradation of organics on surface waters is to be determined after ozonation, those die-away tests incorporating additional organic nutrients are less applicable to the practical conditions prevailing in a water treatment plant. If however,

the biodegradability of a specific organic contaminant in the water is to be evaluated separately, simulation of the appropriate environmental conditions by the addition of particular organic nutrients may be advantageous.

In view of the above, the remaining discussion is limited to respirometric biodegradability tests in which the metabolism of the test compound is followed by the measurement of oxygen uptake and the loss of dissolved organic-carbon. After an initial acclimation or lag period, Monod kinetics predict an exponential increase in oxygen uptake in response to increased microbial growth (refer Figure 2.5-1). As the substrate available for growth is depleted the oxygen uptake rate decreases and a plateau is reached corresponding to the maximum utilization of dissolved organic carbon. The decrease in dissolved organic carbon alone is insufficient proof of biodegradation since other removal mechanisms such as surface adsorption on flocs, or precipitation may occur. However biodegradation may be assumed if, in addition to carbon removal, oxygen is consumed or carbon dioxide is produced in greater quantities than expected from the respiration of the inoculum alone.

While a positive result in these tests clearly indicates biodegradability, a negative result is not

conclusive evidence of persistence. Other factors such as the test technique, toxicity effects, lack of cometabolism or essential nutrients, absence of the required bacterial species or insufficient acclimation may explain such a result.

The Evaluation of Biodegradability by Respirometric Methods

Many of the numerous respirometric techniques for determining biochemical oxygen demand have been reviewed by Jenkins (1960) and Montgomery (1967). The principles of measurement involved in these methods, and more recent improvements, are summarized in Table 2.5-1 together with reference to a number of applications, and their various advantages and disadvantages. The numbered references referred to in Table 2.5-1 are given below. All the methods listed conform to the die-away test classification previously mentioned. Although continuous-flow respirometers have been described by O'Brien and Clark (1967), Ribbons (1969), and by Thiele and Schmit (1969), their operation is complex and they are not considered here.

The limited usefulness of the BOD_5 method for evaluating biodegradability is well known (Busch, 1971). This is especially the case for refractory substrates where appreciable lag periods and reduced rates of biodegradation are expected. In such substrates, a continuous record of oxygen uptake, as attained through respirometry,

TABLE 2.5-1

RESPIROMETRIC METHODS FOR DETERMINING BIOCHEMICAL OXYGEN DEMAND

Test Method Operating Principle	Specific Test Method	Sample Volume (ml)	Reference[a]	Performance Characteristics
METHODS WITHOUT CONTROLLED OXYGEN SUPPLY				
1. Depletion of Dissolved Oxygen or oxygen source	B.O.D. Dilution with or without polarographic D.O. sensor	300	(1) (2) (8) (9)	Slow, unsuitable for studies on biological treatability, inhibition and toxicity. Poor simulation of practical treatment conditions. Reproducibility difficulties commonly encountered. Depletion of a dissolved oxygen donor e/g/ chlorate may be complicated by nitrate interference.
2. Manometric tests, measuring a decrease in system gas volume or pressure	Sierp apparatus and modifications	100-300	(2)	Limited sensitivity (≈ 7 mgO_2/ℓ). These methods characterized by decreasing oxygen concentration in the air space unless pure O_2 is used.
	Gilson apparatus		(2) (3)	Improved sensitivity, micrometric measurement of oxygen volume added.
	Barcroft and similar variations	3-750	(2) (4) (5) (6)	Unaffected by barometric pressure, simultaneous differentiation of O_2 uptake by 2 compounds possible, good reproducibility although water condensation in manometer capillary may be a problem. Maybe applied to low rates of respiration over long periods.
	Burchard	275	(2) (11)	Direct barometric pressure read from aneroid barometer, low sensitivity.
	Warburg	4-75	(2) (7)	Minimum O_2 demand measurable is 5 mg/ℓ to 5% precision. Reproducibility comparable to BOD dilution.
METHODS INCORPORATING A CONTROLLED OXYGEN SUPPLY				
1. Supply from an oxygen storage vessel.	Snaddon & Jenkins Wilson	750-5000	(2)	Apparatus bulky and elaborate. Incorporates external CO_2 scrubbing for high uptake rates. Supply regulated by pressure or volume changes.
2. Oxygen generation by a manometric electrolysis cell.	Young and modifications	1000	(2) (9) (10) (12)	Constant O_2 pressure maintained, automatic with continuous recording of O_2 uptake. May be designed to be independent of atmospheric pressure. Possible interference from ozone depending on choice of electrolyte. Suited to long term biodegradability studies.
	Sapromat		(2) (13)	Independent of barometric pressure, replicates agreement ±5%. Similar to method of Young.

[a]Refer to the text in Section 2.5.3 for a listing of these references.

is quite important.

The limitations and factors affecting respirometric oxygen uptake, as discussed by Montgomery, et al., (1971) and Young and Baumann (1976), must be considered when interpreting the results of treatability studies. In addition to those factors affecting microbial activity, as outlined in Section 2.5.2, consideration should be given to the following:

(i) The oxygen production rate and mass transfer characteristics of the system.

(ii) The gas composition above the sample.

(iii) The influence of barometric pressure.

(iv) Accuracy and precision of the method.

(v) The continually changing microbial population due to required adaptation to declining substrate type or concentration.

References Incorporated in Table 2.5-1

(1) Standard Methods, 1975.

(2) Montgomery, 1967.

(3) Parisod and Schroeder, 1978.

(4) Shulze and Hoogerhyde, 1967.

(5) Wheatland and Lloyd, 1955.

(6) Tebbut and Berkun, 1976.

(7) Brink and Meyers, 1965.

(8) Busch, 1971.

(9) Young and Affleck, 1974.

(10) Young and Baumann, 1976.

(11) Burchard, 1966.

(12) Bridie, 1969.

(13) Liebmann and Offhaus, 1966.

2.5.4 Relative Biodegradability of Organic Compounds

The relative biodegradability of various organic compounds has been the subject of numerous studies. Bacteria may adapt to a wide variety of environmental conditions and degrade many types of compounds. However the complex biochemical interactions involved make difficult to confirm or refute the concept that all organic compounds may be biodegraded if the right organisms, enzymes, nutrients, and environmental conditions for growth are provided. Certainly some compounds degrade more readily than others. Alexander (1965) reports humic substances remain in the soil for hundreds of years. Varying degrees of degradation are discussed by Thom and Agg (1975), Pitter (1976), and Gilbert and Watson (1977). Organic compounds may be classified as those readily degraded, those degraded after suitable acclimation, and those resistant to biochemical oxidation. The biodegradability of a particular compound may be related to its structure, concentration and toxicity.

However all bacterial decomposition systems are self-limiting and even readily degraded compounds like glucose are not degraded completely (Painter, 1973). Biodegradation is not possible without bacteria, and yet the presence of bacteria implies there is an organic residue.

Chemical factors which effect biodegradability are molecular size, solubility, tertiary branching, the nature, position, and number of substituents in the molecule and the presence of heterocyclic atoms. The effect of chemical structure has been summarized by Painter (1974). For instance the chain length is important; alkanes tend to be degraded more readily the longer the chain length up to 12 carbon atoms, and branching increases the resistance to oxidation. Similarly the results of Chambers, et al. (1963) indicate molecular structure may be related to the resistance of bacterial degradation. Substituents in the benzene ring may increase biodegradability as in the case of mono-alkyl substitution, however further methyl substitution beyond toluene decreases biodegradability. Groups such as hydroxyl, aldehydes, and carboxyls, generally increase susceptibility while halogens and nitro groups decrease it. In addition dichlorophenols were shown to be more resistant than monochlorophenols.

Of particular concern in this research is the

degradation of natural and synthetic substances found in sources of drinking water. In contrast to readily biodegradable materials such as glucose and glutamic acid (Busch and Myrick, 1961), these compounds are more resistant to aerobic microbial stablisation. The type of compounds and in some cases the specific degradation rates using acclimated inoculums have been summarized by some authors. For example the degree and rate of degradation, based on COD removal, was evaluated quantitatively for 123 organic compounds by Pitter (1976) using the organic substance as the sole source of carbon and an inoculum of adapted activated sludge. A number of compounds, including nitroaniline, exhibited low or zero removal of COD.

Inadequate treatment of industrial wastes may result in surface water contamination. Based on thirty day BOD studies, Porter and Snider (1976) and Weeter and Hodgson (1977) reported very slow degradation rates for textile dyes and effluents. Young and Affleck (1974) studied the persistence of nitroaniline isomers from a pharmaceutical waste in respirometers, over a 180 day period, and concluded ortho-nitroaniline is essentially non biodegradable.

Thompson, et al. (1960) and Helfgott, et al. (1977) developed biochemical treatability indices for comparing

the biodegradability of various compounds. The Biotreatability Index (BTI) proposed by Thompson, et al. (1960) is defined by a relationship based on the rate of oxygen uptake, carbon removal, and the enzymatic activity of the bacteria present. Considerable analysis is required for determining the index for each compound compared to the technique described by Helfgott, et al. (1977). This method is based on respirometric studies to determine the 'ultimate' Biochemical Oxygen Demand (BOD_u) and the measurement of the Ultimate Oxygen Demand, UOD (a combination of Total Oxygen Demand, TOD, and the equivalent oxygen demand of the nitrogen present). A refractive index R.I., is thus defined:

$$R.I. = \frac{BOD_u}{UOD}$$

This index is designed to predict the persistence of a compound in an aqueous environment based on the test conditions. Humic substances were found to resist degradation almost completely (R.I. = 0.0) compared to readily degradable compounds such as glucose (R.I. = 0.9).

2.5.5 The Effect of Ozone Pretreatment on Biodegradation

Changes in the Total Organic Carbon (TOC) and Chemical Oxygen Demand (COD) of organic compounds after chemical oxidation with ozone are commonly determined.

However the biodegradability of the products thus formed are less frequently reported. The investigations in which this effect has been assessed indicate that ozone pre-treatment of refractory organic compounds may result in the formation of more readily biodegradable products. These studies may be described under the following three categories; the ozonation of:

(i) Industrial Effluents.

(ii) Treated Municipal Wastewater.

(iii) Potable Water Supply.

Typically process streams from the first two categories are characterized by relatively concentrated organic substances while the TOC concentration of water for potable supply is generally less than 10 mg/ℓ.

Industrial Effluents

Comparatively high ozone doses are required for significant oxidation of the more concentrated organic compounds in these effluents. Batch reactor bio-oxidation studies by Yocum, et al. (1977) showed that ozonation improved the biodegradability of a number of industrial effluents containing biorefractory compounds such as toluene diisocyanate and ethylene dichloride. Relatively concentrated samples (100 - 1000 mg/ℓ TOC) of effluent were ozonated extensively (0 - 7 mg O_3 consumed per mg TOC) in

a 20 ℓ turbine reactor prior to aeration in the batch reactors. Biodegradability evaluation was based on the reduction of TOC and five day Biochemical Oxygen Demand (BOD_5) over a three day period using an acclimated seed. A substantial increase in the BOD_5/TOC ratio was observed, although interpretation of the results is confused by air stripping of both the reactant and products during ozonation and aeration in the batch reactors.

Based on their experiments Suzuki, et al. (1976, 1978) concluded ozonation contributed to improving the biodegradability of several water-soluble polymers, including polyethylene glycol (PEG) and poly (vinyl alcohol), PVA. No significant change in biodegradability was observed for polyacrylamide although the molecular weight was decreased over eight hundred fold after 0.9 gms of ozone was consumed per gm of polymer. However almost complete biodegradation of PEG resulted after similar ozonation. Aqueous solutions of the polymers (0.4%) were ozonated at pH 12 and room temperature. The concentration was reduced to 0.2% for the biodegradability tests and the pH buffered at pH 7.4. Biodegradability was based on the variation of molecular weight distribution and the progressive change in TOC over a 30 day period in 500 mℓ shaker flasks at 37°C, using river bed mud as an inoculum.

Kwie (1969) evaluated the effect of ozone pre-treatment on biodegradability for three wastestreams from a synthetic polymer plant. The ozonation of sodium 8-alkyl naphthalene sulphonate-2 (SANS) was of particular interest because of its extreme resistance to biodegradation. Concentrated solutions (>750 mg/ℓ SANS) were ozonated (1-3 mg O_3/mg TOC) in a 100 mℓ reaction vessel and oxygen uptake subsequently determined using a Warburg respirometer. No improvement in biodegradability was observed over the 130 hr. incubation period, however it was noted this may be attributed to the use of an unacclimated sludge inoculum in the test.

The biodegradability of industrial dye wastes (250 - 2200 mg/ℓ TOC) before and after ozonation was studied by Netzer and Miyamoto (1975) in batch aeration reactors using activated sludge as the inoculum. Although it is concluded that ozonation enhances the biodegradability of these wastes no data is given to support this claim.

Following the ozonation of dilute aqueous solutions of aminobenzoic acid (1 mmole/ℓ) and naphthalene-2, 7-disulphonic acid Gilbert (1977) determined the ratio BOD_5/COD to increase with increasing ozone dose (0-16 mg O_3/mg TOC).

Treated Municipal Wastewater

Refractory organic compounds in municipal wastewater after secondary treatment have become more biodegradable after ozonation. Sontheimer, et al. (1977, 1978) showed ozonation improved the biological treatment, and hence removal of Dissolved Organic Carbon (DOC) and COD across a sand filter (refer to Figure 2.5-3). Increasing ozone dose resulted in decreased COD/DOC ratios as further material was oxidised. However changes in the ozone dosage between 5 and 25 mg/ℓ did not result in very different performance and it was concluded the optimum ozone dose ranged between 0.2 and 0.5 mg O_3/mg DOC. Ozone consumption was optimum at pH 7 to 8. Furthermore the most efficient ozone use can be achieved with slow reaction and low ozone gas concentration. Similarly Guirguis, et al. (1978) observed substantial organic removal from chemically treated municipal effluent when this was pre-ozonated prior to sand filtration.

In contrast Nebel, et al. (1972) observed an average 15% decrease in the BOD_5 of municipal wastewater after secondary treatment and ozone doses between 5 and 15 mg/ℓ. On occasions the BOD_5 increased, and this was attributed to the presence of refractory organics from an industrial source.

Evans and Ryckman (1963) investigated changes in the biodegradation of a known concentration of alkylbenzene

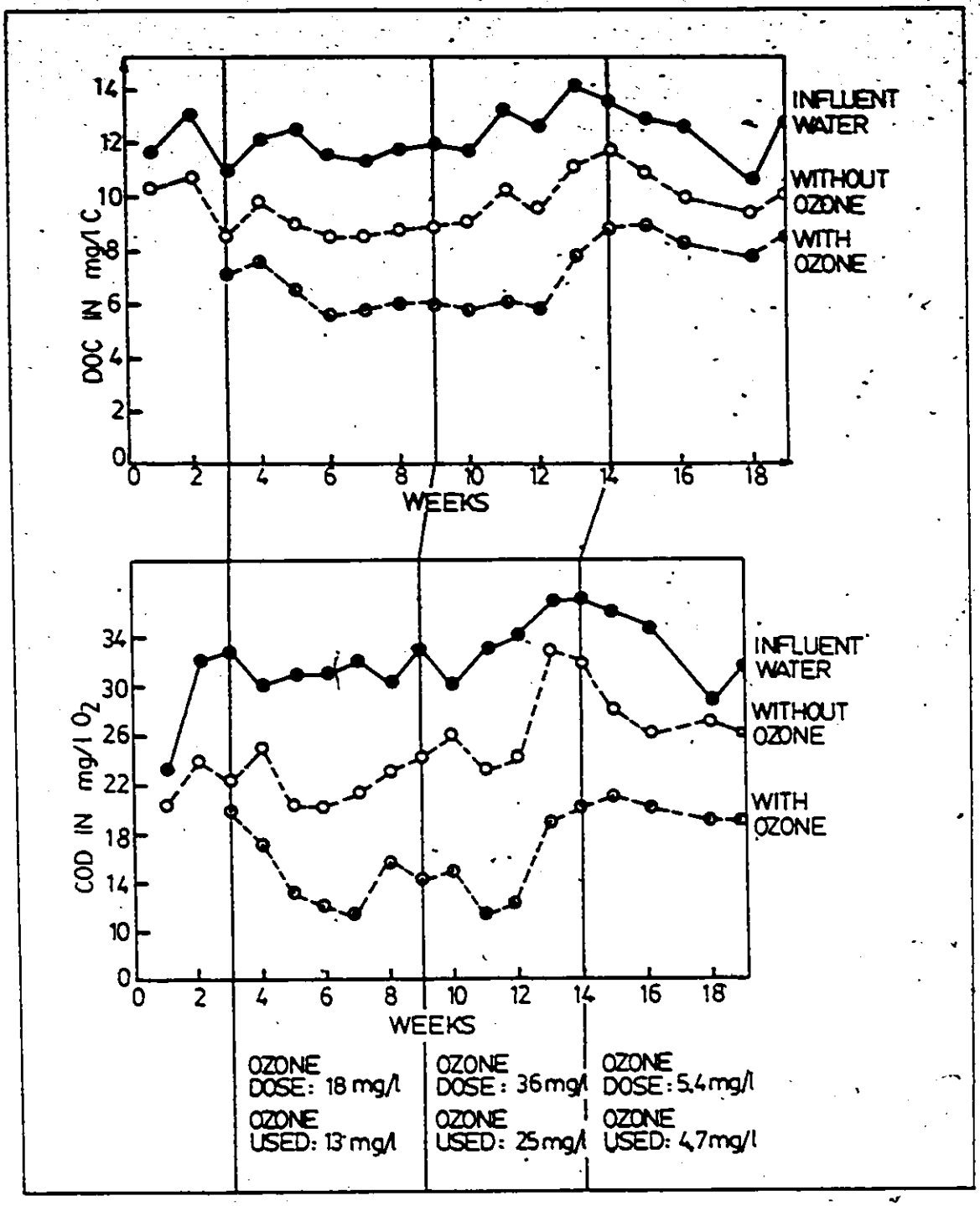


FIG.2.53 DISSOLVED ORGANIC CARBON (DOC) AND CHEMICAL OXYGEN DEMAND (COD) REMOVAL FROM A SECONDARY EFFLUENT THROUGH A BIOLOGICAL SAND FILTER WITH AND WITHOUT OZONE (Sontheimer, 1976)

sulphonate (ABS) in municipal effluent after secondary treatment, after partial oxidation by ozone. The biodegradability was determined by observing the progression of BOD, (probably using the dilution technique). Increasing ozone consumption over the range 0.1-2.1 mg O_3/mg COD resulted in decreasing BOD_{20}. However the BOD_5 of a 10 mg/ℓ solution of ABS increased with increasing ozone dose to a maximum corresponding to the complete removal of ABS (11 mg O_3/mg ABS). The BOD_5/COD ratio simultaneously increased with increasing removal of ABS. A more concentrated solution (50 mg/ℓ ABS in distilled water) was ozonated and utilized as the substrate in a Warburg respirometer. The original concentration of ABS inhibited the activated sludge inoculum, but as the ozone dose was increased this inhibitory action rapidly decreased and the substrate resulted in bacterial growth. The rate and extent of biodegradation was improved by increased ozonation. Janicke (1977) similarly showed improved biodegradation of detergents after ozonation.

Potable Water Supply

In a number of European water treatment plants ozone is applied prior to granular activated carbon adsorption columns (Rice, et al., 1979) to improve the removal of organic material. (Sontheimer, et al., 1978, Kuhn, et al.

1976). Organic removal is greater than that attributable to the independent effects of ozone and granular activated carbon (Hopf, see Rice,et al,1979). It is considered the removal results from the combined effects of adsorption and increased biological activity. Ozonation of the surface water, it is claimed, results in the formation of more biodegradable compounds which are then degraded by bacteria on the carbon surface. For example research at Bremen, West Germany, has shown that activated carbon which removed 1 mg/ℓ TOC before ozonation removed 3 mg/ℓ TOC after ozonation (Eberhardt , et al., 1975).

Benedek (1977) notes that the formation of more polar compounds such as carboxylic acids and aldehydes after the ozonation of surface water organics may reduce the equilibrium carbon adsorption capacity, thus partially offseting the benefits of improved biodegradability. In studies at the Morsang-sur-Seine Water Treatment Plant in France, pre-ozonation (controlled to a residual between 0.3 to 0.4 mg/ℓ O_3) resulted in only a small improvement in biodegradation.

After the ozonation of relatively concentrated solutions of humic substances (>200 mg/ℓ HS) found in surface waters, Mallevialle, et al. (1977) and Hartemann, et al. (1977) observed that the BOD_5 increased after ozonation. In the former case extended ozonation resulted in a decreasing BOD_5/TOC ratio.

In summary these studies are characterized by one or more of the following experimental shortcomings:

(i) Relatively high initial concentrations of the organic substrate to be ozonated.

(ii) Extended ozonation, often several hours, resulting in high ozone doses.

(iii) Ozone treatment at controlled pH levels.

(iv) Biodegradability assessment based on the BOD_5 method.

(v) Indirect biodegradability evaluation, such as improved organic removal by granular activated carbon.

(vi) Short term biodegradability studies, usually on the order of several days or less.

An independent assessment of ozone pretreatment effects on the biodegradability of refractive substances found in sources of drinking water, using long term respirometric studies conducted on dilute aqueous solutions, at low oxidant doses, short contact times, and with no pH control may be more directly related to the ozonation practices typical of most water treatment plants.

The aim of this study is to evaluate the effect of ozone on biodegradation under these conditions.

SECTION 3

THE DESIGN OF A LABORATORY OZONE CONTACTOR

The design and construction of a laboratory ozone contactor was required to ozonate aqueous solutions from a number of sources. In this section the specific design criteria, mass transfer characteristics, and performance evaluation are presented for the contactor built for this study.

3.1 DESIGN OBJECTIVES

The design of the specific contacting system is based on the following objectives:

(i) To simulate an ozone contacting system typical of full scale water treatment plant installations.

(ii) To maximize ozone absorption from the gas phase to the liquid phase.

(iii) To oxidize biorefractory organic compounds at low concentrations in aqueous solution.

(iv) To minimize the loss of volatile components during ozonation.

(v) To provide sufficient capacity for subsequent analysis of the ozonated samples.

(vi) To limit sample contamination by using appropriate materials of construction for gas and liquid contacting.

(vii) To incorporate equipment for the measurement of applied gas flow rate, pressure, and ozone concentration.

3.2. EQUIPMENT DESCRIPTION

3.2.1 Basis of Selection

As previously reviewed a variety of systems have been used or suggested for the ozone/water contacting process. Of these contactors the most common in water treatment practice is the gas sparged column dispersing tower. By comparison with other configurations this device combines efficient ozone absorption with low power expenditure. For most practical situations ozone is optimally generated from air at concentrations in the order of 12-15 mg per litre of gas. In typical installations the applied ozone dose ranges from 2 to 10 mg per litre of liquid over a 3 to 15 minute contact period.

In preference to a turbine agitated system initially evaluated, a bubble column was designed in which near equilibrium quantities of ozone could be transferred to the aqueous phase by providing a suitable gas sparger and sufficient rise height for the bubbles. The mass transfer model used to evaluate this design is described in Section 3.2.3.

In view of operational reproducibility and sample requirements a batch ozone contactor was considered advantageous. With this system, the extent to which biorefractory organics in aqueous solution are oxidized may be varied by

altering the liquid retention time in the contactor. The oxidation of these organics at concentrations typically found in surface waters is considered to be reaction rate limited (See, et al., 1976; Miller, et al., 1978), as opposed to mass transfer limited. Therefore an ozone residual may be expected in the liquid phase. Excessive decomposition of ozone may be avoided by optimization of the gas flowrate and ozone concentration. In addition gas stripping of any volatile components formed during ozonation may be reduced by employing low gas flowrates and maximizing ozone absorption.

A minimum contactor volume of 24 ℓ is required to provide a sufficient quantity of treated sample for analysis.

3.2.2 Apparatus

The ozonation apparatus designed and built for this study is shown in Figure 3.4-1.

Process Description

A pressure regulated (0.7 bar) stream of high quality air (TOC <0.1 ppm as methane) flows from a gas reservoir (K1) to a silica gel drying column (K2) before passing to a PSI ozone generator (K3). A constant gas flow to the generator ensures relatively uniform concentrations of ozone in the product stream. The required flow of ozonated air is then metered (C2 & C_3) to the contacting

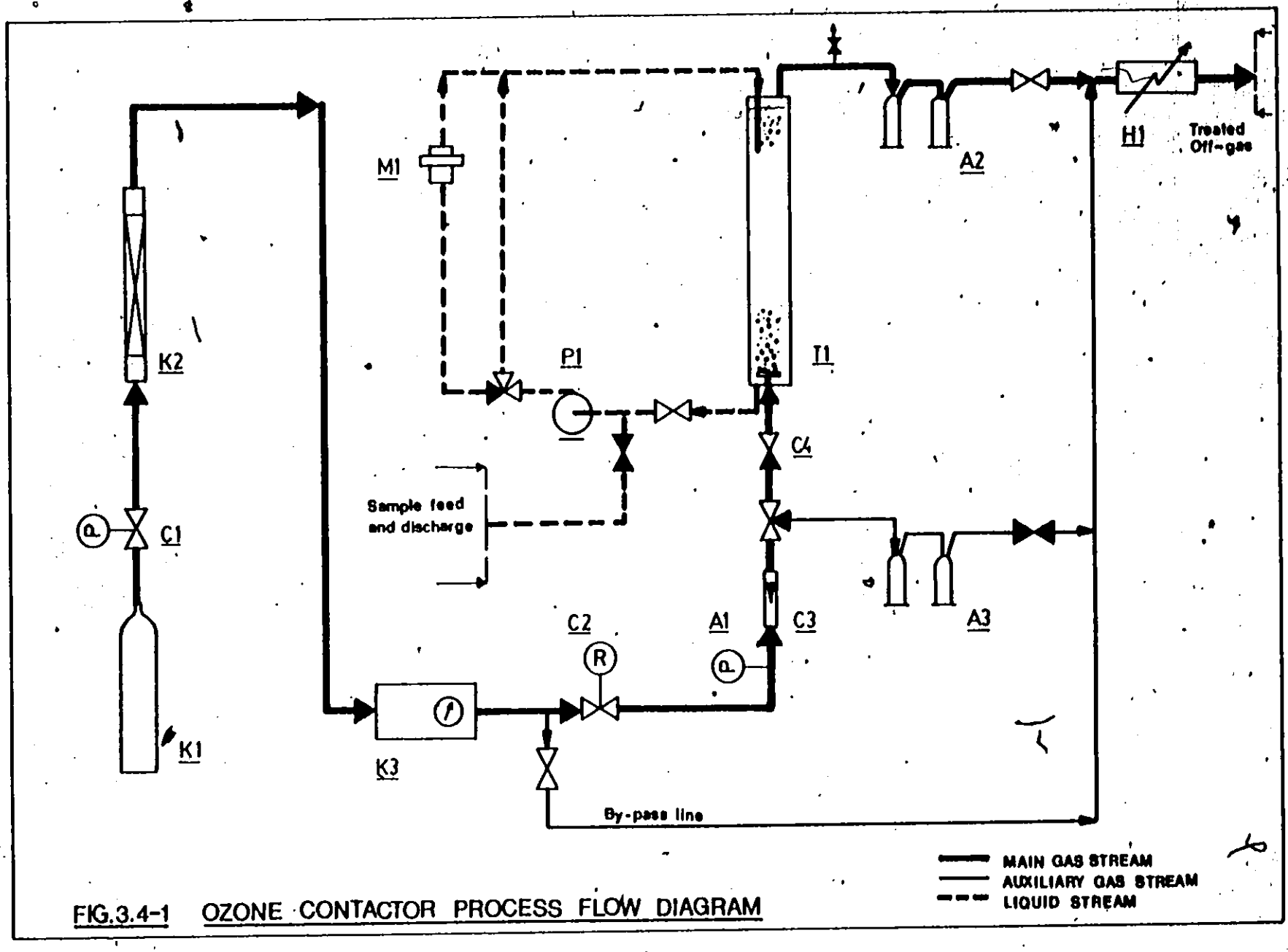


FIG.3.4-1 OZONE CONTACTOR PROCESS FLOW DIAGRAM

column (T1), or feed gas sampling apparatus (A3), while any remaining gas is neutralized in a heat exchanger (H1) and subsequently exhausted to atmosphere. Similarly the ozone concentration in the contactor off-gas is analysed prior to exhausting (A2).

The liquid sample to be ozonated is pumped (P1) into the contacting column through a pressure filter (M1). Once the contactor is loaded the valves are adjusted to by-pass the filter and continuously recirculate the liquid countercurrently. Countercurrent liquid recirculation ensures conditions analogous to full scale operation while simultaneously providing more uniform liquid mixing. After treatment is complete the sample is drained from the column by gravity.

To limit sample contamination and ozone side reactions, all pipework and fittings contacting ozonated gas and water streams are constructed of stainless steel, glass, or teflon. Pipe lengths are minimized to reduce the effect of spontaneous ozone decomposition.

Equipment List

Item	Description	Materials	Duty/Size
T1	Ozone contacting column complete with coarse sintered glass gas sparger and base mounts.	Glass S.S. end plates	305 cm x 10.2 cm ID
P1	Micropump Magnetic drive recirculating pump	S.S. case Teflon impeller	25 ℓ/min @ 0 Head

Item	Description	Materials	Duty/Size
K1	High quality air reservoir	M.S.	8 m^3
K2	Silica gel drying column and filter		
K3	PSI Ozone generator	Teflon, S.S.	2.5 gms/hr
M1	Pressure filter	S.S.	5 ℓ/min @ 0 press. drop.
H1	Externally heated ozone decomposition chamber	Aluminum	1 ℓ, 280°C
C1	Single stage pressure regulator	Brass	0-4.2 bar
C2	Fine metering valve	S.S.	
C3	Gilmont No. 3 Rotameter with glass float	Glass	10 ℓ/min
C4	Back pressure valve	S.S.	
A1	Pressure Gauge	Brass	0-1 bar
A2	Contactor off-gas ozone gas scrubbers (2)	Glass	500 mℓ x 2
A3	Contactor feed gas ozone gas scrubbers (2)	Glass	500 mℓ x 2

3.2.3 Mass Transfer Design

Mass Transfer Model

The mass transfer design is to provide for the maximum utilization of ozone in the contactor. As reviewed in Section 2.3.1, the change in gas phase ozone concentration across the contactor depends on numerous factors.

An ozone mass balance for the system is shown below:

$$\text{Ozone Input} - \text{Ozone Output} = \text{Ozone accumulation} + \text{Ozone decomposition} + \text{Ozone reaction}$$

Assumptions: The mass transfer model for the batch contactor design is based on the following assumptions:

(i) Mass transfer may be described by the film theory.

(ii) The liquid phase is completely mixed. Gas bubbles produced at the base of the column agitate the liquid and in most cases produce complete mixing (Valentin, 1967; Hill and Spencer, 1975). The degree of mixing depends on the gas flowrate and may be characterized by an apparent liquid diffusion coefficient. Siemes and Weiss (1959) found values ranging from 7 cm^2/s at superficial gas velocities of 2 cm/s to 70 cm^2/s at 7 cm/s, which indicates good mixing even in relatively narrow columns. In addition liquid recirculation promotes more uniform mixing.

(iii) Plug flow contacting of the rising gas bubbles.

(iv) The gas flow rate and film diffusivity is unaffected by the dissolution of air.

(v) The rate of ozone decomposition is proportional to the three halves power of the ozone concentration in the pH range 6-9. First order decomposition kinetics are also widely reported (Section 2.2.1) at these pH values. The effect of these two mechanisms is discussed below. In both cases it is assumed there is no reaction in the liquid film.

(vi) Direct chemical reaction of ozone with organic substances is proportional to both the ozone and substrate (S) concentrations, as described by Hoigné (1977). The literature (Section 2.4.3) suggests that many organic compounds, and in particular refractory substances, react with the aqueous decomposition products of ozone rather than directly with ozone. In this case, as for the ozonation of 'organic free' water, this reaction term may be deleted.

(vii) The rate of ozone decomposition through the gas sparger is small.

(viii) The fractional holdup of liquid outside the column in the recirculation loop is negligible.

(ix) The mass transfer coefficient (k_ℓ) is not enhanced by chemical reaction.

Equations: Based on the above assumptions the residual zone concentration (C), in the bulk liquid of a batch

gas sparged column contactor may be expressed as a function of time (t) by:

$$\frac{dC}{dt} = \frac{G}{V}(1 - e^{-PDh})\left(y_o - \frac{K_H C}{P}\right) - k_d C^{3/2} - k_r[S]\cdot C \quad (1)$$

where, G Inert gas flowrate (mole S^{-1})

V Reaction volume (cm^3)

P Contactor pressure (atm)

h Column liquid depth (cm)

D $f(G,V,h,k_\ell,k_g, a, K_H)$

y_o Mole fraction of ozone in the applied gas stream

k_d Ozone decomposition constant $(moles/cm^3)^{-\frac{1}{2}} S^{-1}$

k_r Reaction 'constant' $(cm^3/mole)S^{-1}$

[S] Concentration of reacting substrates.

The derivation of this equation and its solution by the fourth order Runge-Kutta method is presented in Appendix 1. Also shown is the fraction of ozone in the gas phase (y), as a function of the rise height (x):

$$y = \frac{K_H C}{P} + \left(y_o - \frac{K_H C}{P}\right) e^{-PDx} \quad (2)$$

The solution of these equations for various dimensional and operational conditions forms the basis for the chosen design.

Model Predictions: By way of example Figures 3.2-1, 3.2-2 show the respective variation in liquid and exhaust gas

ozone concentrations with time for the operating conditions summarized in Table 3.2-1. These predictions are based on the ozonation of distilled water for which mass transfer and decomposition constants are available from the literature (Hill and Spencer, 1975; Shambaugh and Melnyk, 1976; Kuo, et al., 1976). Since the solution is free of organics the reaction term in (1) is equal to zero. i.e. $k_r[S].C = 0$.

For the case of first order ozone decomposition, the term $k_d C^{3/2}$ in (1) is replaced by $k_d'C$. The rate constant k_d' may be calculated from Stumm (1954) to be $0.0129\ s^{-1}$. The model predictions of liquid ozone residual as a function of time for the two reaction mechanisms are compared in Figure 3.2-3. For the given conditions a higher ozone residual is predicted using first order ozone decomposition. However in view of the uncertainty associated with the decomposition constants reported (Section 2.2.1), this disparity is not considered significant.

When compounds which react directly with ozone are present in the water sample, the model Equ. (1) predicts a further reduction in the liquid ozone residual and hence the exhaust gas ozone concentration. As ozonation proceeds the organic substrate is further oxidized to form a variety of products, with different reaction kinetic characteristics. To predict the effect these reactions have on the ozone

TABLE 3.2-1

MODEL PARAMETER VALUES FOR OZONE ABSORPTION IN DISTILLED WATER AT pH 7.2 AND 8.3

Variable				pH 7.2		pH 8.3	
Volumetric interfacial area, a (cm^2/cm^3)*				0.12	0.35	0.12	0.35
Decomposition rate constant, k_d ($(moles/cm^3)^{-\frac{1}{2}}.S^{-1}$)**				1.091	1.091	483	483
Common Variables							
Reactor Press. P, (atm)	Temp. T, (^oC)	Reactor Vol. V, (cm^3)	Liquid depth h, (cm)	Gas flowrate G, (moles/S)	O_3 input mole fract.	Mass transfer Coef. k_ℓ (cm/s)***	
1.25	20	2.4×10^3	2.96×10^2	7.81×10^{-4}	7.64×10^{-3}	1.42×10^{-2}	

* For a fractional gas hold up of 0.015 and spherical bubbles of 7.5 mm and 2.5 mm diameter (Estimate based on typical bubble size from gas spargers).

** Kuo, et al., 1976.

*** Hill and Spencer, 1975; Shambaugh and Melnyk, 1976.

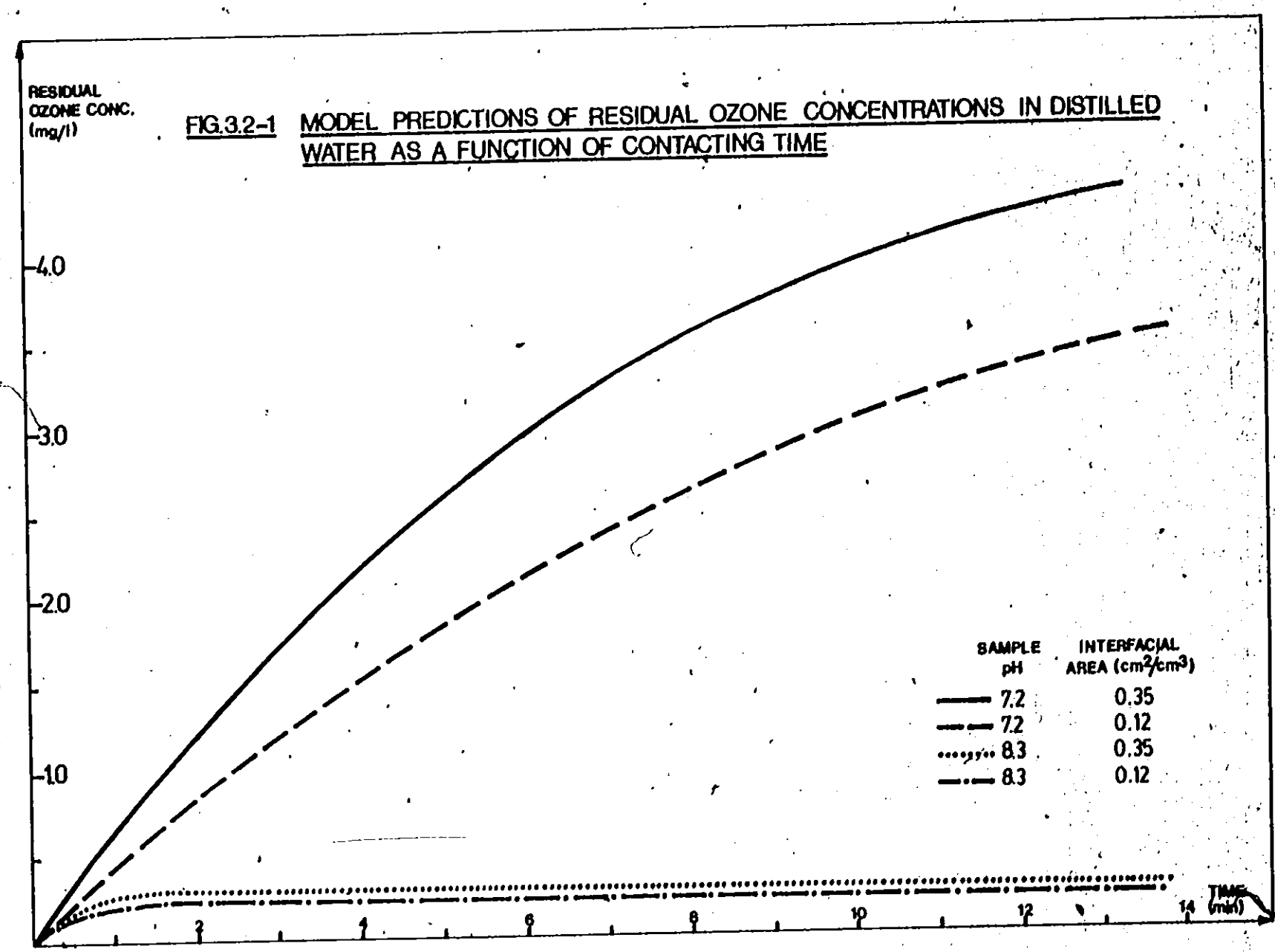


FIG.3.2-1 MODEL PREDICTIONS OF RESIDUAL OZONE CONCENTRATIONS IN DISTILLED WATER AS A FUNCTION OF CONTACTING TIME

FIG.3.2-2 OZONE CONCENTRATION IN THE CONTACTOR EXHAUST GAS AS A FUNCTION OF TIME FOR THE OZONATION OF DISTILLED WATER

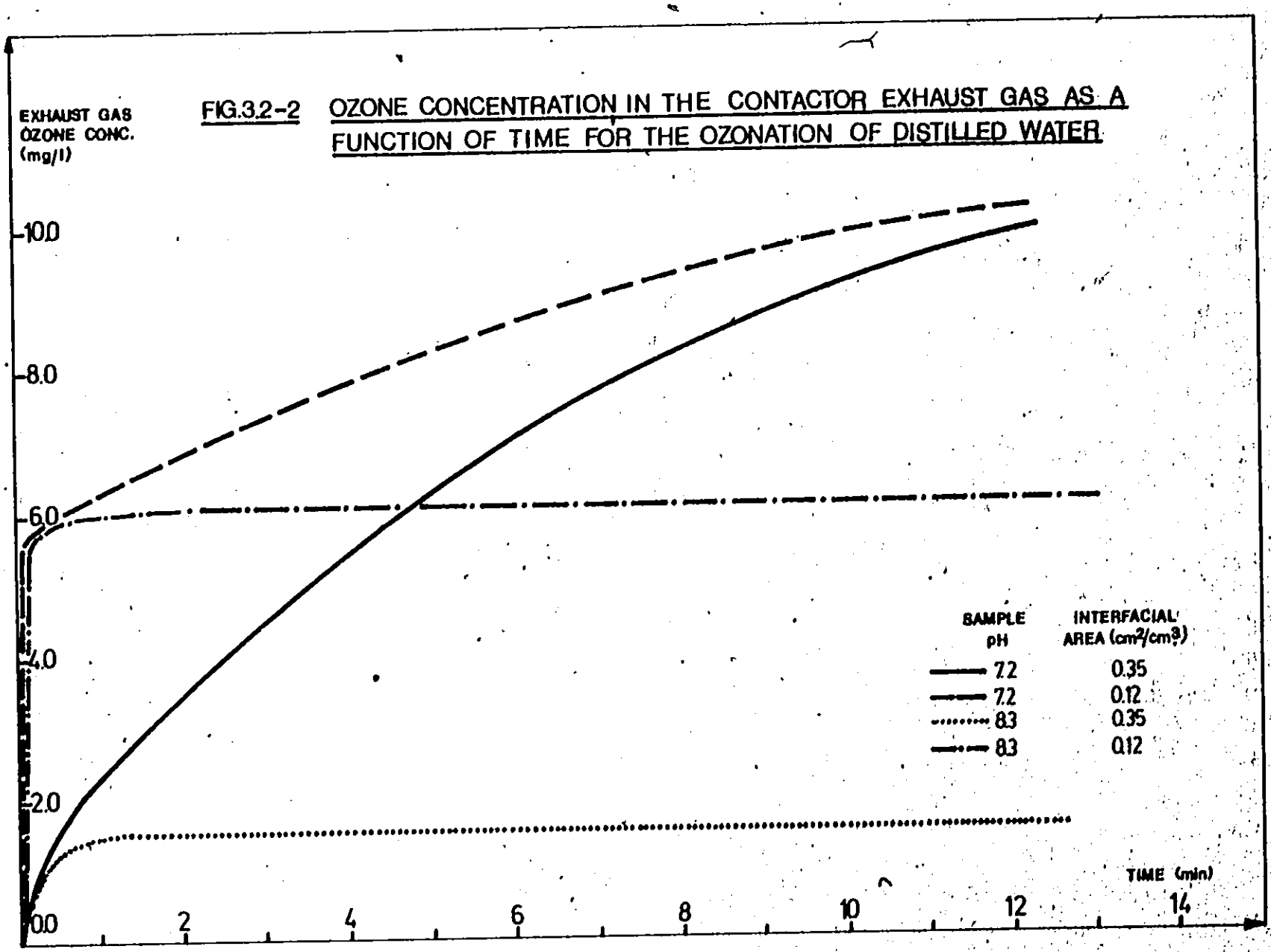
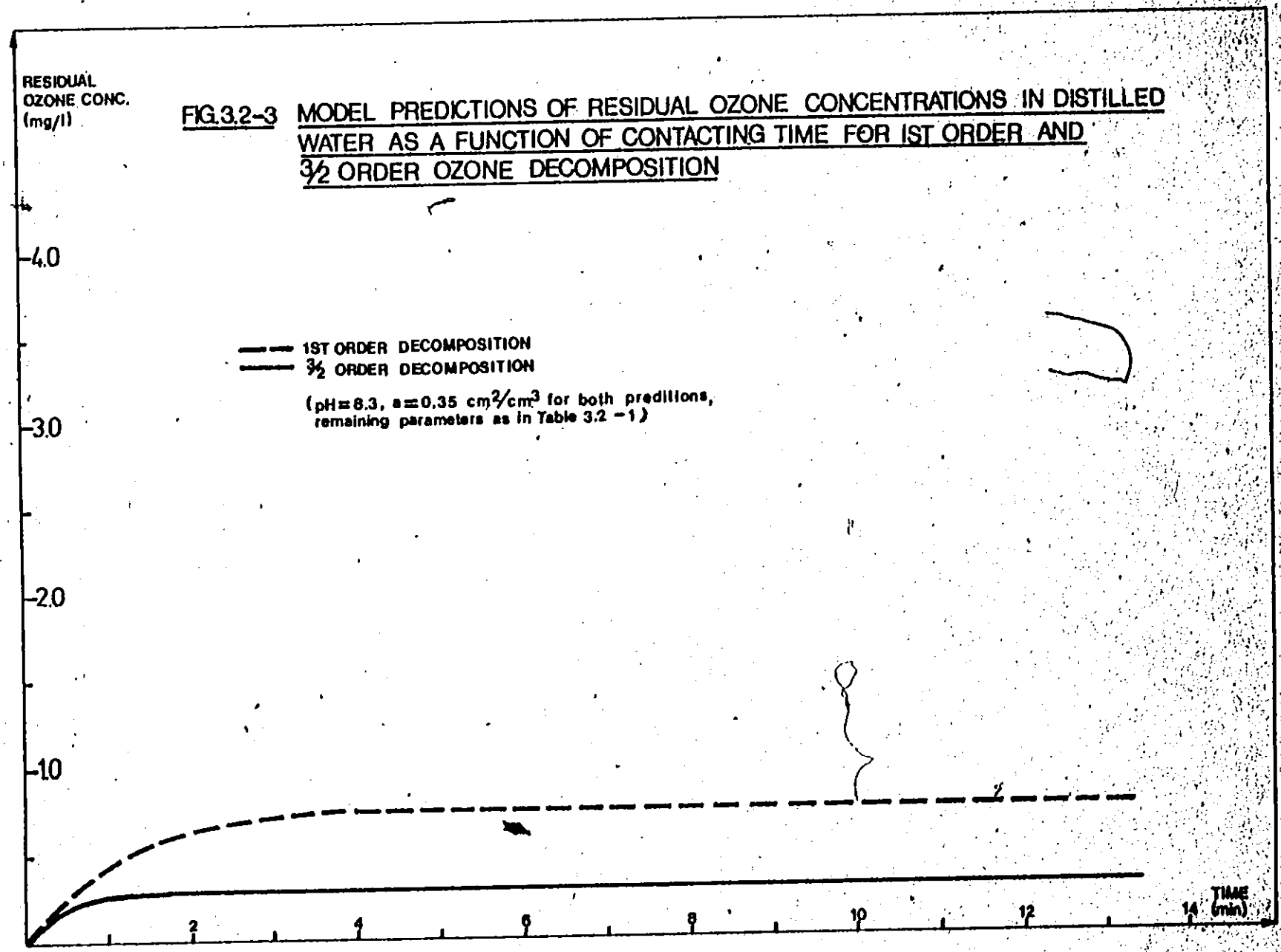


FIG.3.2-3 MODEL PREDICTIONS OF RESIDUAL OZONE CONCENTRATIONS IN DISTILLED WATER AS A FUNCTION OF CONTACTING TIME FOR IST ORDER AND 3/2 ORDER OZONE DECOMPOSITION



residual would require the development of a more complex model.

pH Effects

As shown in Figures 3.2-1 and 3.2-2 the residual ozone concentrations in the liquid and column exhaust gas respectively, is very significantly affected by pH. At higher pH values the increased decomposition rate is such that lower residual concentrations result in both streams.

Bubble Size Effects

The effect of bubble size, and therefore interfacial area, on the residual liquid ozone concentration appears to be less significant than pH for the range examined, (see Figure 3.2-1). As expected ozone absorption is improved by increasing interfacial area (see Figure 3.2-2).

In tall columns some coalescence of gas bubbles is inevitable, although this is inhibited by the presence of surface-active agents and electrolytes (Benedek, 1970; Eckenfelder and Barnhart, 1961). Calderbank, et al. (1964) postulated two distinct regions of coalescence behaviour:

(1) A region in which the rise velocity is a strong function of bubble diameter and significant coalescence occurs (bubble diameter less than 3 mm).

(2) A region of constant bubble rise rate (3-7 mm dia.) in which coalescence is much less frequent.

Thus as the average bubble size increases there is a tendency towards uniformity of gas bubble size, and hence gas plug flow. However at high gas flows this effect is less significant due to increased liquid turbulence and greater coalescence. Kolbel, et al. (1962) observed an approach to plug flow at superficial gas velocities of about 2-4 cm/s.

Contactor Dimensions

Based on an evaluation of the above model, in excess of 90% ozone abosrption is expected in a 300 cm high column with a 250 μ pore diameter gas sparger during the ozonation of river water. Furthermore this depth is comparable with many full scale installations. A 10.2 cm dia. column provides the required sample volume and allows for adequate liquid mixing with recirculation. The relative superficial gas velocity for a gas flow of 1 ℓ/min. and a recirculation rate of 25 ℓ/min. is 5.3 cm/sec.

3.3 EQUIPMENT PERFORMANCE

3.3.1 Ozone Generation

Ozone is generated at a concentration of 12-15 mg/ℓ for an air flow of 3.2 ℓ/min. When 1.05 ℓ/min of this stream is supplied to the contactor the applied ozone dose to a 24 ℓ water sample is 0.6 mg O_3/ℓ.min. On this basis the applied ozone dose is fixed for a given contact time. For example a contact time of 3.5 mins implies an ozone dose of 2.1 mg/ℓ. These conditions are analogous to full scale ozonation practice.

3.3.2 Contactor Performance

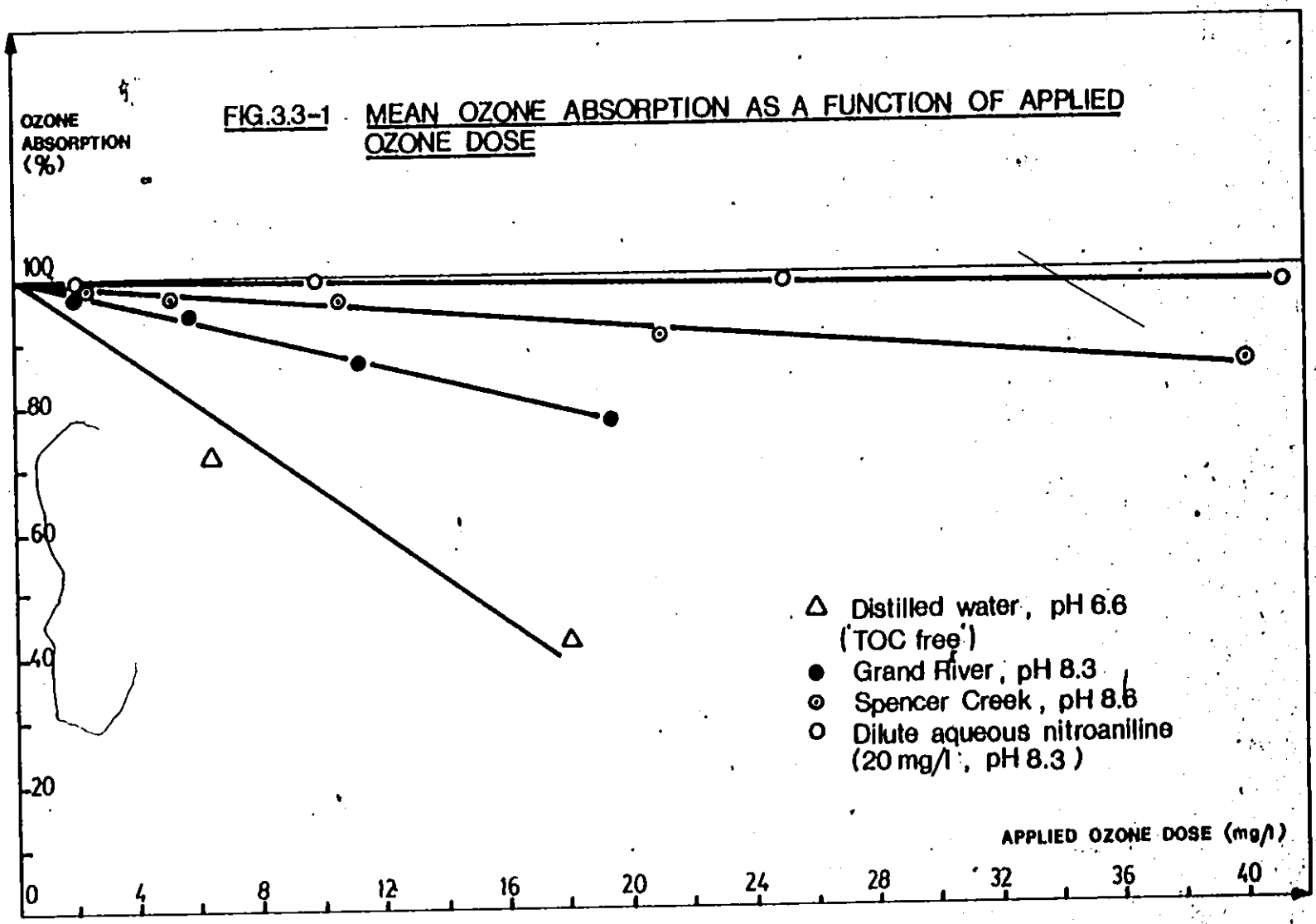
Contactor k_ℓ a Value

The contactor mass transfer characteristics without ozone reaction were determined on the basis of reaeration with air. A value of 0.0029 sec^{-1} was calculated for $k_\ell a$. Details of the method and calculation procedure are presented in Appendix 2.

Ozone Absorption

The absorption performance of the ozone contactor for four aqueous solutions is shown in Figure 3.3-1, based on information tabulated in Appendix 4. For the most part greater than 90% absorption of ozone may be achieved.

FIG.3.3-1 MEAN OZONE ABSORPTION AS A FUNCTION OF APPLIED OZONE DOSE



The decreasing absorption at higher ozone doses may be attributed to both a closer approach to the steady state ozone residual and the reduced effectiveness of organics oxidation for the longer contact times.

In Figure 3.3-2 the liquid residual ozone concentration is plotted for three solutions. The presence of organics has a marked effect on the residual, implying in part the direct reaction of these with ozone. The residual measured for the ozonation of Grand River water signifies a reaction rate limited system. However in the case of aqueous nitroaniline no residual was detected, thus indicating ozone mass transfer limitations.

Comparison of Model Predictions and Experimental Data

Model predictions are based on the ozonation of distilled water, for which values of the decomposition constant are given in the literature. These predictions cannot be compared directly with those results obtained from the ozonation of 'organic free' tap water, (tap water filtered through activated carbon) because of interferences from inorganic ions such as carbonates. However it is interesting to note that the experimental residuals plotted in Figure 3.3-2 for 'organic free' tap water are higher than the model predictions for distilled water at the same pH, as shown in Figure 3.2-3. The model may be fitted to this experimental data with an ozone decomposition constant (k_d)

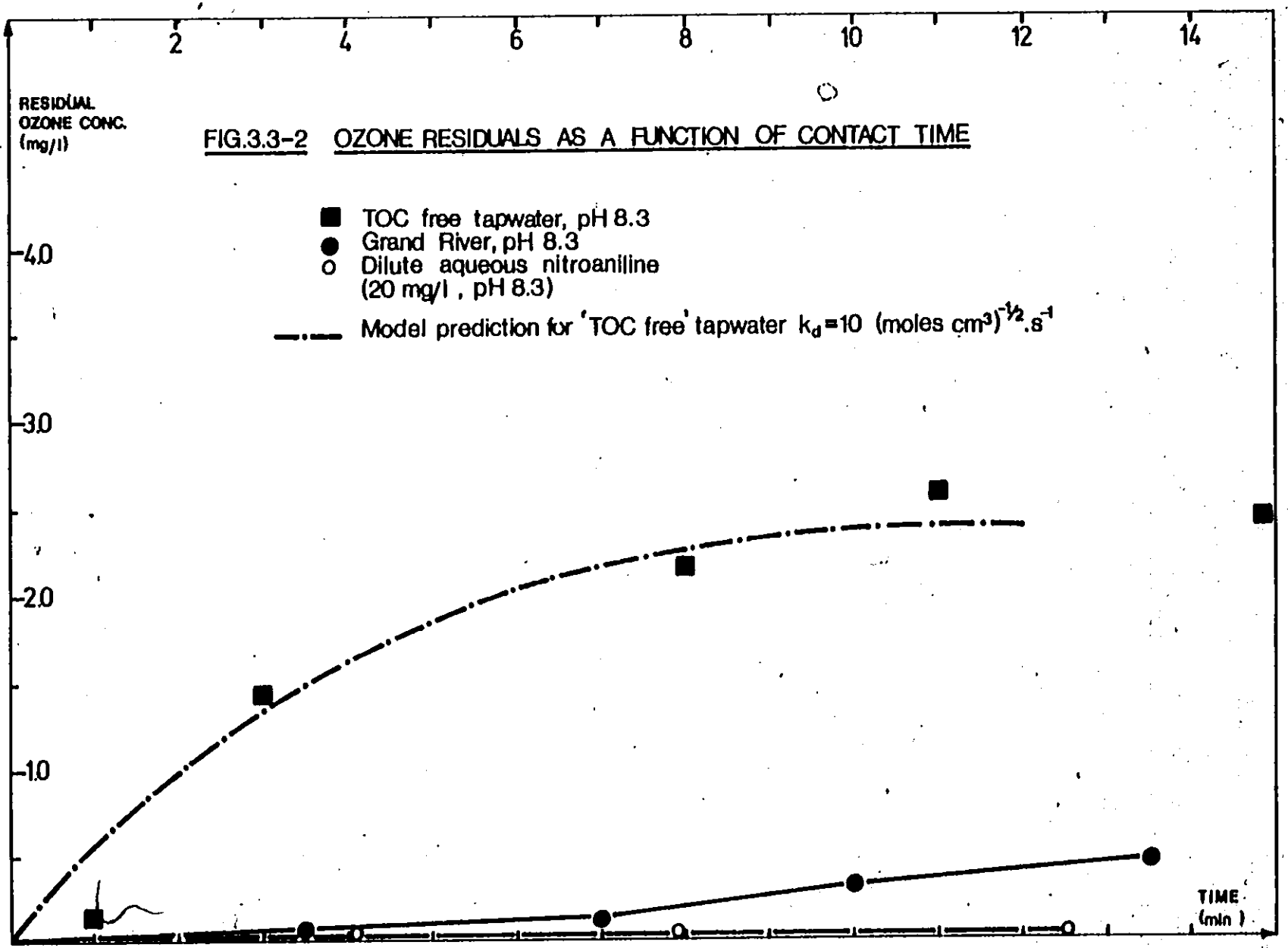


FIG.3.3-2 OZONE RESIDUALS AS A FUNCTION OF CONTACT TIME

of - 10 $(moles/cm^3)^{-\frac{1}{2}} \cdot s^{-1}$.

Although insufficient kinetic data is available for predicting the ozone residual in the presence of organics, the reduced residuals measured after the ozonation of Grand River water and aqueous nitroariline solutions are in qualitative agreement with the model. As the organics are oxidized the ozone residual is expected to increase to the steady state concentration exhibited by 'organic free' water.

SECTION 4

EXPERIMENTAL

4.1 WATER SOURCES

Ozonation and biodegradation studies were conducted on samples from three water sources:

4.1.1 Grand River, Southern Ontario

The dilute organic compounds in water samples taken from the intake of a drinking water treatment plant on this river originate from both natural sources and those associated with typical agricultural and urban land use. At the sampling location the river is approximately 20 m wide, and downstream from a number of industrial and domestic wastewater discharges. Water samples were generally turbid and light green in colour.

4.1.2 Spencer Creek, Southern Ontario

This surface water flows through the Beverly Swamp area of Wentworth County, Ontario. Clear and light brown in colour, it is characterized by a relatively high concentration of humic substances (Lawrence, 1979). The supply is free of point sources of domestic or industrial wastewater.

4.1.3 Dilute Aqueous Nitroaniline Solution

Nitroaniline is a highly coloured aromatic compound used as an intermediate in manufacturing dyestuffs, pharmaceuticals, and a number of synthetic organic chemicals. The biorefractory nature of nitroaniline isomers has been demonstrated by Pitter (1976), and Young and Affleck (1974). In particular ortho-nitroaniline has been detected in river water (Meijers and Van der Leer, 1976) and shown by Young and Affleck (1974) to be essentially non biodegradable. Para-nitroaniline was reported to be degraded with sufficient acclimation (Chambers, et al., 1963; Young and Affleck, 1974; Young and Baumann, 1976).

4.2 TREATMENT PROCEDURE

Each water source was subjected to the treatment steps as displayed in Figure 4.2-1.

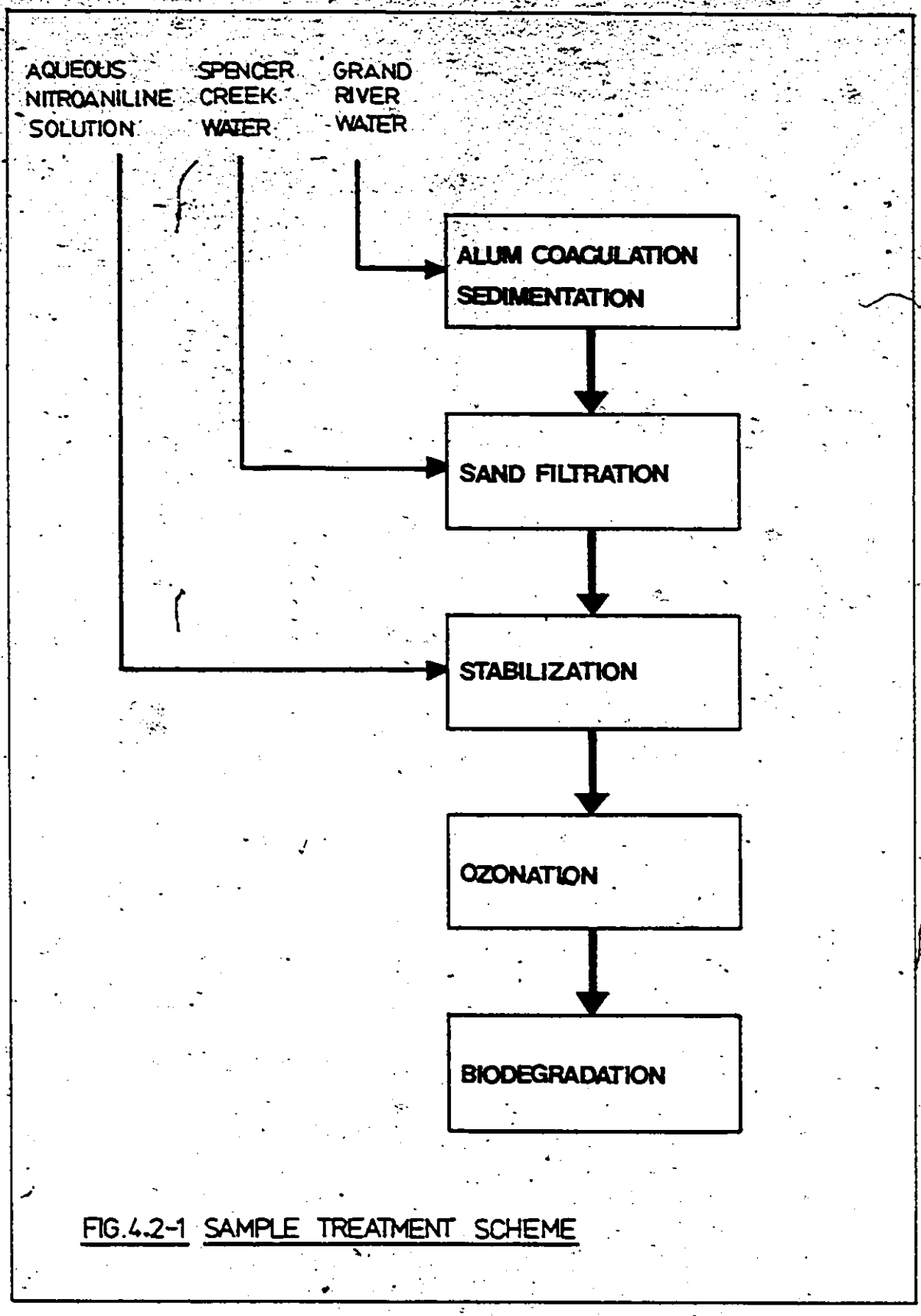


FIG.4.2-1 SAMPLE TREATMENT SCHEME

4.3 SAMPLE PREPARATION

4.3.1 Collection, Coagulation, and Filtration

(i) Grand River: Pretreatment of this water simulated common practice in a drinking water treatment plant. In this manner only those organics not removed in these processes would be ozonated.

Water samples (200 ℓ) pumped from the river were flocculated with 50mg/ℓ Alum in a rapid mixer, settled, and gravity sand filtered through 30 cm of water treatment plant filter (Ottawa type, approx. 0.6 mm dia effective size).

Collection was conducted at approximately monthly intervals between August 1978 and March 1979.

(ii) Spencer Creek: Pretreatment of 200 ℓ samples consisted only of gravity sand filtration as above.

(iii) Dilute Nitroaniline Solutions: Dilute concentrations of nitroaniline isomers (approx. 20 mg/ℓ) were made using Hamilton tap water previously filtered through activated carbon for TOC removal.

4.3.2 Stabilization

All samples for ozonation and biodegradability evaluation were continuously aerated at 20°C, by low pressure air spargers, until a constant TOC level could be maintained. This level is considered to be commensurate with stablized microbiological activity and the presence of only bio-refractive organic substances.

4.4 OZONATION

Test samples (24 ℓ) of the stablized water were pumped into the batch contactor through a glass fibre filter. Ozone, generated in a dry high purity air stream at 0.7 bar, was then bubbled through the column at a constant rate for a specified contact time. For all experiments the gas flow rate to the contactor was maintained at 1.05±0.02 ℓ/min (wet test meter calibration data for the No. 3 Gilmont rotameter is tabulated in Appendix 3) and the ozone concentration controlled, typically within 12-14 mg/ℓ, using the gas bypass. Consequently a specific contact time corresponds to a particular applied ozone dose.

The mean ozone concentration in the gas phase exhausted from the column throughout the contact period was determined after ozone absorption in 500 mℓ potassium iodide (KI) solution; two scrubbers were used in series to ensure complete absorption, however in most instances one was sufficient. Similarly a facility for bypassing the contactor allowed for the determination of ozone in the applied gas. By scrubbing this latter stream for 5 min before and after ozonation a mean initial ozone concentration could be calculated for the run.

During ozonation, and for 5 min thereafter, the liquid phase was continuously recirculated countercurrent to the gas flow. The column was then drained into cleaned glass vessels and samples subsequently prepared for analysis and respirometric studies.

4.5 RESPIROMETRY

4.5.1 Apparatus

Biodegradability of the test compound was evaluated in respirometric apparatus especially constructed for this study, based on the manometric electrolytic technique developed by Young and Clark (1965). The apparatus, as illustrated in Figure 4.5-1, consists of four major parts:

(i) A 10 ℓ narrow mouthed glass reaction vessel and a 65 mm 'egg' shaped teflon coated magnetic stirring bar. The drive unit for the magnetic stirrers was insulated from direct contact with the reactor base with a 6 mm thick layer of plywood to avoid heat transfer. A similar mixing level was visually adjusted for each reactor to ensure near equilibrium concentrations of dissolved oxygen and to retain the micro-organisms present in suspension.

(ii) An adaptor unit containing wetted pellets of potassium hydroxide to absorb metabolically produced carbon dioxide from the atmosphere above the sample.

(iii) A manometric electrolysis cell using 0.7N H_2SO_4 as the electrolyte. 0.7 N H_2SO_4 is preferred over the use of more concentrated

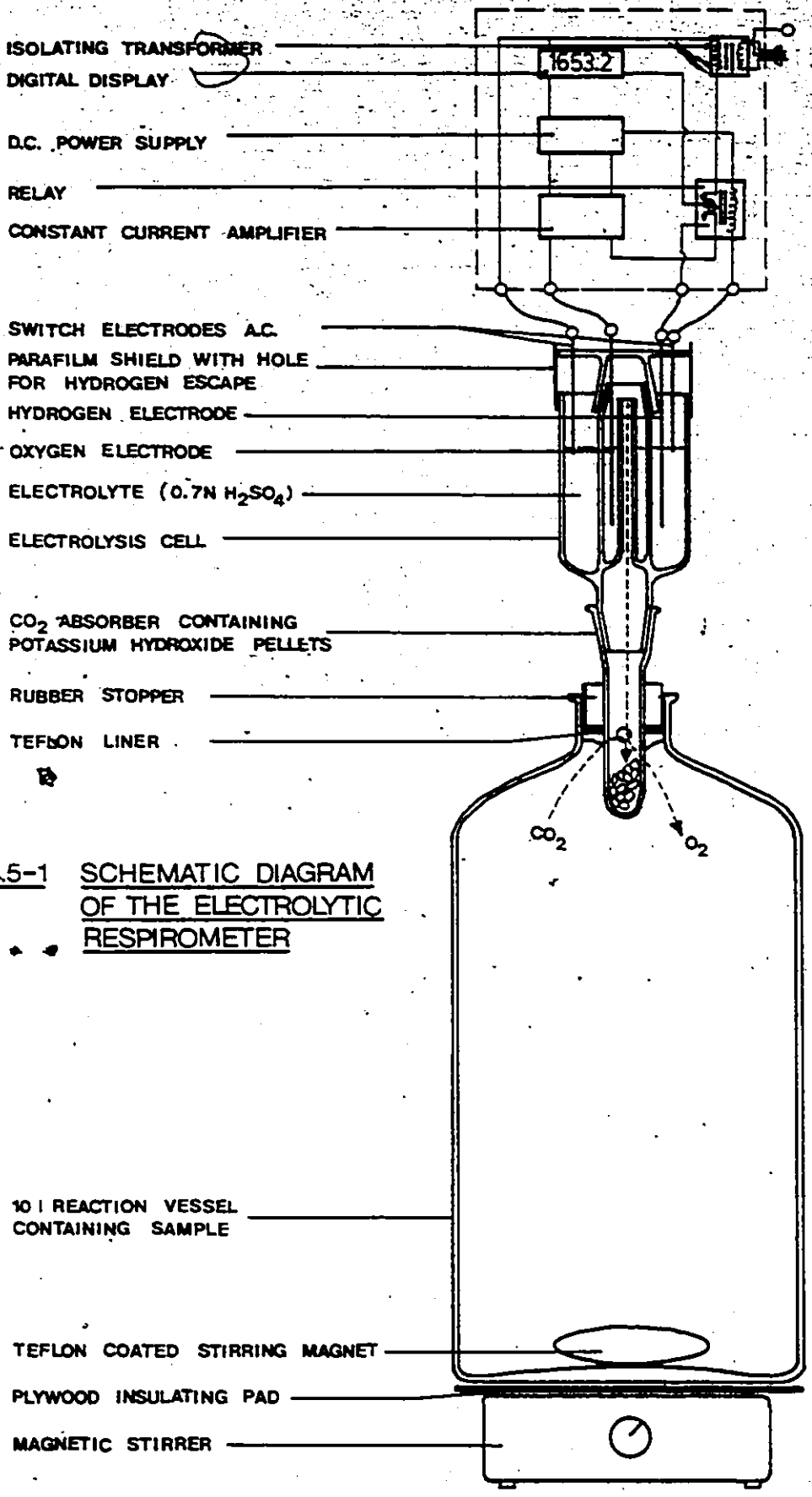


FIG 4.5-1 SCHEMATIC DIAGRAM OF THE ELECTROLYTIC RESPIROMETER

solutions due to the possible formation of ozone. Similar problems may be encountered when copper sulphate is used as the electrolyte (Montgomery, et al., 1971).

In response to pressure changes detected by two platinum electrodes (1 mm dia.) in an A.C. circuit oxygen is generated at the anode of two other platinum electrodes in a constant current D.C. circuit. In this way a constant partial pressure of oxygen is maintained in the atmosphere above the sample. A parafilm shield, enclosing the upper section of the cell, was fitted to minimize electrolyte evaporative loses. An airtight seal is provided for fitting the various parts with the use of small quantities of silicone grease.

(iv) A control console containing all the necessary power supplies, circuitary, controls and integrated digital readout. Similar systems are reported in the literature by Bridie (1969) and Montgomery (1971).

Cell operation is characterized by the bacterial consumption of oxygen, causing a reduction in the gas volume above the sample and a fall in the electrolyte level in the outer annulus of the cell. When the level falls below the

switching electrodes an A.C. circuit is broken, which in turn activates the electrolytic current and a timer. Electrolysis continues to generate oxygen under constant current (201 mA) conditions until the A.C. circuit is remade, at which point the timer is also switched off. The oxygen consumed by the bacteria may then be calculated knowing the electrolyte current and its duration. A cell current of 201 mA over a 1 min period corresponds to the evolution of 1 mg of oxygen.

An increase in barometric pressure also reduces the volume of the gas phase and causes more air to dissolve. The electrolytic cell then supplies oxygen to restore the orginal volume of the gas and hence an equivalent amount of oxygen must be subtracted from the indicated demand to correct the error. The reverse is the case for a decrease in barometric pressure although the switching mechanism will not operate unless there is an equivalent change in biochemical oxygen demand (BOD). The correction for barometric pressure is given as: (Wheatland and Lloyd, 1955)

$$W_{O_2} = \left[V_s \cdot \alpha + \frac{273}{273+T} \cdot V_A\right] \frac{\Delta P}{760} \cdot \frac{1.43 \times 1000}{V_s}$$

where

W_{O_2} Oxygen required to correct the measured BOD, mg O_2/ℓ

V_A Volume of air space above sample, ml

V_s Sample volume, ml

ΔP Barometric pressure change, mm Hg

T Temperature, ^{o}C.

The necessity for these corrections only becomes significant for very low strength samples. Then the error may be minimized by reducing the air space above the sample to a minimum.

4.5.2 Equilibration

The reaction vessel was filled with an ozonated water sample and placed in a constant temperature room adjusted to $20.0 \pm 0.1^{o}C$. With the vessel contents vented to atmosphere the sample was agitated for approx. 15 hours to achieve thermal equilibrium and ensure the complete disappearance of ozone. Following the addition of inorganic nutrients and the bacterial inoculum, also at $20^{o}C$, the carbon dioxide absorber and electrolysis cell were positioned and the appropriate electrical connections made. With a syringe the volume of electrolyte in the cell was adjusted to the critical level for switching before sealing the interior gas phase.

The volume of gas above the sample was minimized to reduce the effects of barometric pressure changes. Each reactor was filled to a prescribed level to provide an initial air space of 90-100 ml above the sample after assembling the absorber and cell.

4.5.3 Inoculum

As indicated in the literature the ozonation of humic substances and aromatic compounds result in the formation of many oxidized intermediates. To increase the chances of bacterial acclimation the dilute solutions of these compounds were inoculated with diverse populations of bacteria. Furthermore to prevent significant contamination of the test sample itself a low TOC inoculum was required.

The inoculum source depended on the particular substrate under consideration. Nevertheless in each case the inoculum, or seed, was filtered through Whatman No. 2 paper to reduce the predator micro-organism population without seriously affecting the viability of the bacteria (Busch, 1958). The volume of filtered inoculum added to each respirometer was 100 mℓ, i.e. approx. 10 mℓ/ℓ.

(i) Grand River and Spencer Creek: Seed used for these studies was settled activated sludge from the Dundas Water Pollution Control Plant. Although the viability of seed from this source may have varied for successive runs, the same seed was added to all respirometers within a specific run.

(ii) Dilute Nitroaniline Solutions: In this case the seed was obtained from laboratory draw and fill activated sludge reactors. A mixed

substrate consisting of raw sewage, glucose, ethanol, and the particular nitroaniline isomer of concern was fed to the reactors over a 21 day period prior to acquiring seed for the respirometry studies.

4.5.4 Nutrient Requirements

Excluding nitrogen and phosphorus it was assumed that sufficient concentrations of all the remaining nutrients required for biological growth were already present in the water samples ozonated. Although low concentrations of phosphorus were measured in the waters its availability for bacterial growth, especially after alum flocculation was unknown. Also predominant forms of nitrogen were determined as nitrate or Total Kjeldahl Nitrogen (TKN) rather than ammonia. Therefore to ensure that organic carbon was the growth limiting nutrient ammonia nitrogen and orthophosphate were provided according to the ratio C:N:P of 100:5:1. It is noted that excessive nitrogen was undesirable due to the possibility of nitrification. In one experiment, as noted in Section 6, the biodegradability of Grand River water was evaluated without nutrient addition.

4.5.5 Calibration

To check the above procedure determinations were

made using 100 mg/ℓ glucose solutions. The results were then evaluated by comparison with values of Biochemical Oxygen Demand reported in the literature.

Settled and filtered (Whatman No. 2) activated sludge from the Dundas plant was used as the inoculum and inorganic nutrients were added in the proportions given in Standard Methods (1975).

4.6 ANALYSES

This section describes the analytical techniques used in this study.

4.6.1 Soluble Organics Analysis

The effect of ozone treatment, and the subsequent biodegradability assessment of the test compound, was in part based upon changes in the concentration and composition of soluble organic substances. Those organic compounds not retained by a 0.45 μ cellulose nitrate filter are defined as soluble. To reduce sample contamination filters were pre-soaked in distilled water and washed with 300 mℓ of the sample to be analyzed. Sufficient sample was then collected in cleaned glass sample bottles for the following analyses:

(i) Total Organic Carbon (TOC)

The TOC concentration was determined by a Dohrman model DC54 Ultra Low Total Organic Carbon Analyzer (Dohrman Co., Santa Clara, California). In principle this instrument converts all forms of organic carbon into methane which in turn is quantitatively measured by a Flame Ionisation Detector (FID). On the basis of triplicate determinations TOC levels may be considered accurate to ± 25 μgms/ℓ.

(ii) Chemical Oxygen Demand (COD)

The potassium dichromate method of Maier (1973) was used for COD measurement. An acidified dichromate solution oxidizes the sample in a closed flask at 160°C and the extent of oxidation is subsequently determined by titration with Ferrous Ammonium Sulphate. A detection limit of 0.2mg/ℓ is claimed and the estimated precision is ±3%.

(iii) Ultraviolet Absorbance (UV)

Sample aromaticity and the concentration of other ultraviolet absorbing structures was measured with a Bausch and Lomb (Bausch and Lomb Co., Rochester, New York) Spectronic 21, model UV-D Spectrophotometer. A 10 cm long sample cell was used and at an absorbance of 0.400 the error is specified as 0.003.

4.6.2 Nitrogen

To assess the extent of nitrification in the respirometric studies nitrite and nitrate concentrations were determined at the start and completion of incubation. In some instances ammonia nitrogen and Total Kjeldahl nitrogen (TKN) were also measured. Samples were analyzed by colorimetric methods using two Technicon Auto Analyzers (Technicon Corp., Tarrytown, New York) which were set up for Technicon Industrial Methods 19-69 W and 35-69 W.

4.6.3 Biochemical Oxygen Demand (BOD)

Relative biodegradability was also evaluated on the basis of long term oxygen uptake experiments. The biochemical oxygen demand of the ozonated water samples was continuously recorded with the respirometric apparatus previously described. Oxygen uptake information obtained from duplicated respirometry studies on ozonated water samples was compared with that obtained on non-ozonated water and a control, containing low TOC water, inorganic nutrients and the appropriate inoculum (Low TOC water was produced by the filtration of tap water through activated carbon). Samples were incubated at 20°C for periods of 12-35 days.

4.6.4 pH, Temperature, Colour

(i) pH: A Fisher (Fisher Scientific Co., USA) model No. 230 pH/Ion Meter recorded pH values accurate to ± 0.05 units. The instrument was calibrated with standard buffer sol^{ns}.

(ii) Temperature: Temperatures were measured using a mercury bulb thermometer accurate to ±0.05°C.

(iii) Colour: The absorbance at specific wavelengths in the visible range was measured with a Bausch and Lomb Spectronic 21. A scanning spectrophotometer was used to select the appropriate test wavelength.

4.6.5 Ozone

Gas and liquid phase ozone concentrations were determined by the Iodometric method described in Standard Methods (1975). Ozone absorbed into 2% potassium iodide solution liberates free iodine which is quantitatively titrated with sodium thiosulphate using a starch indicator. The minimum detectable concentration is 30 µg/ℓ ozone and the precision of the test is 1%.

4.7 GLASSWARE

To minimize sample contamination following ozonation, glass and teflon materials were used exclusively in subsequent handling and storage vessels. Prior to use, and between runs, these items were cleaned with a concentrated chromic acid solution (Chromerge + Conc. H_2SO_4) to remove organic materials, rinsed three times with distilled water, and inverted so as to drain dry. Special care was adhered to in cleaning the respirometers and the 500 mℓ bottles in which samples were stored prior to analysis.

SECTION 5

OZONATION

5.1 PRE-OZONATED SAMPLE CHARACTERISTICS

All ozonation experiments were conducted using stabilized water samples, as described in Section 4.2.2. In the case of Grand River water, stabilization was preceded by alum pretreatment to simulate common practice in a drinking water treatment plant. In Table 5.1-1 characteristics of all the stablized aqueous samples subsequently ozonated are presented, together with the raw water characteristics for a number of Grand River water samples. Typical changes in Total Organic Carbon (TOC) over the stabilization period are shown in Figure 5.1-1. A small decrease in TOC was recorded for the pretreated Grand River water samples, however no change was observed for the aqueous nitroaniline solutions. The more significant decrease for Spencer Creek samples may be attributed to the degradation of more readily biodegradable organics.

The COD/TOC ratio may be considered indicative of the extent to which any organics present are oxidized. Those ratios presented in Table 5.1-1 highlight the variability in water quality for samples collected from the same source at different times. However similar ratios in the range 1.87-2.92 are noted for Grand River and Spencer Creek samples

TABLE 5.1-1

SAMPLE CHARACTERISTICS PRIOR TO OZONATION

Run No.	Collection Date	TOC (mg/ℓ)	$A_{10\ cm}^{254\ nm}$	COD (mg/ℓ)	pH	Temp. (°C)	COD/TOC
Grand River Raw Water Characteristics:							
1	27. 9.78	-	-	-	8.7	9.5	-
2	18.10.78	-	-	-	8.6	9.5	-
3	1.11.78	-	-	-	8.6	9.1	-
4	19.11.78	-	-	-	8.7	9.0	-
5	8. 1.79	10.27	1.930	-	8.6	0.5	-
6	17. 1.79	8.01	1.810	-	8.6	0.5	-
7	5. 3.79	4.84	1.510	-	8.4	0.5	-
CHARACTERISTICS OF STABILIZED WATER SAMPLES:							
Grand River							
1	27. 9.78	6.15	1.246	11.5	8.4	20.	1.87
2	18.10.78	5.48	1.146	10.7	8.3	20.	1.95
3	1.11.78	-	1.000	11.7	8.3	20.	-
4	19.11.78	3.66	1.083	10.7	8.4	20.	2.92
5	8. 1.79	6.69	1.860	12.7	8.4	20.	1.90
6	17. 1.79	4.64	1.224	10.2	8.3	20.	2.20
7	5. 3.79	3.15	0.894	7.3	8.3	20.	2.32
Mean		4.96	1.208	10.7	8.3	20.	2.19
Std. dev.		1.40	0.313	1.7	0.1	0	0.40
Spencer Creek							
8	19.10.78	9.20	0.455[a]	22.6	8.7	20	2.46
9	6.11.78	8.03	0.417[a]	16.0	8.6	20	1.99
para-Nitroaniline							
10	11.12.78	9.69	0.483[a]	32.2	8.1	20	3.32
ortho-Nitroaniline							
11	26.12.78	10.85	0.738[a]	30.6	8.3	20	2.82

[a]Sample diluted 10:1 prior to measurement.

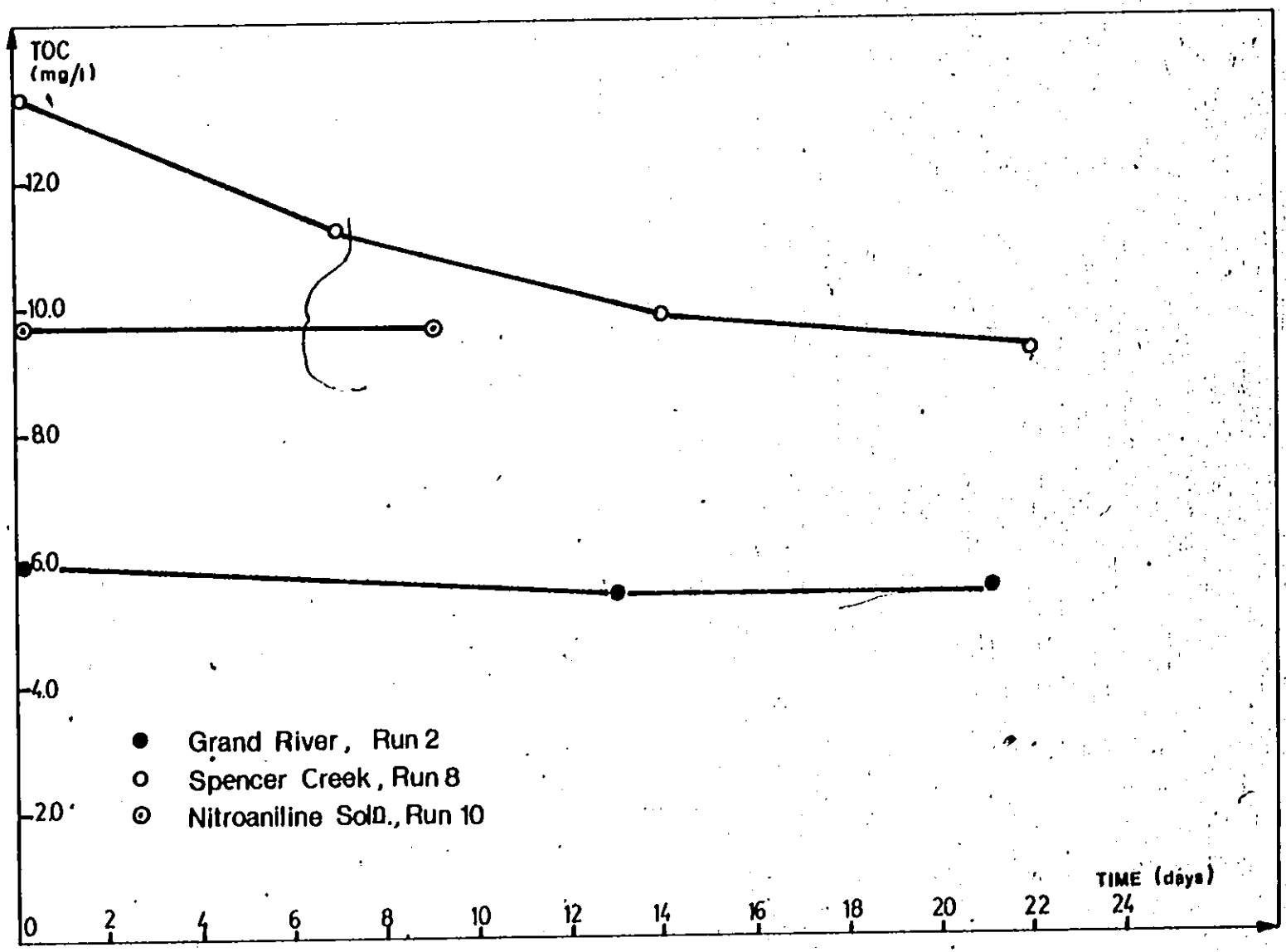


FIG. 6.1-1 TOTAL ORGANIC CARBON (TOC) vs SAMPLE STABLIZATION TIME

while the higher values (2.82-3.32) exhibited by the nitroaniline solutions implies that these organics are less oxidized.

5.2 OZONE RESIDUAL

The decay of ozone residuals was studied to ensure no residual remained on commencing the subsequent biodegradation experiments. In Figure 5.2-1 the residual ozone level in Grand River water, determined 45 sec after ozonation is complete, is shown for different ozone doses. The magnitude of this residual is a function of both the ozone application rate and the significance of reaction sinks; primarily decomposition, and the reaction with organics and inorganic scavengers. Based on the rapid dissipation of a 1.8 mg/l ozone residual, as shown in Figure 5.2-2, ozone levels were assumed to be zero prior to the biodegradation experiments which started approximately 15 hours after ozonation.

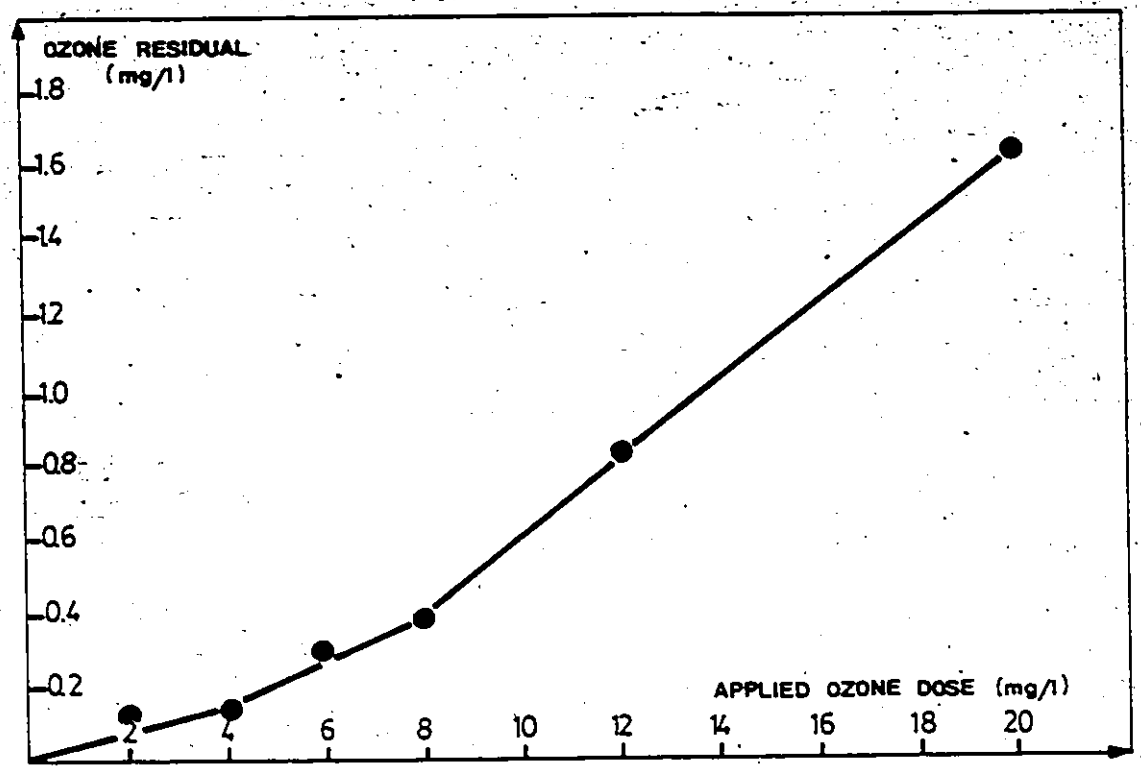


FIG.5.2-1 OZONE RESIDUAL vs APPLIED OZONE DOSE
(Residuals measured 45 sec after completing ozonation, Run 5)

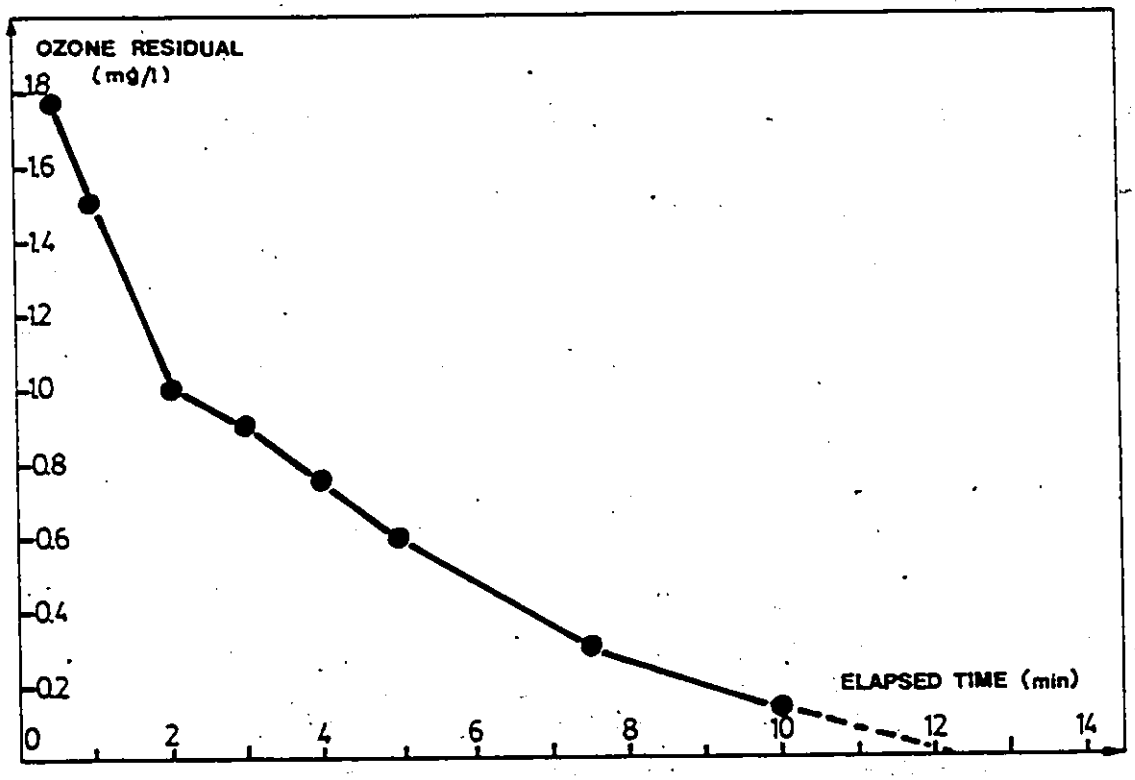


FIG.5.2-2 OZONE RESIDUAL DECAY – Run 5

5.3 ORGANIC REMOVAL

5.3.1 TOC Removal Kinetics

In Figures 5.3-1, 5.3-2 and 5.3-3 Log TOC is shown as a function of ozone contact time for the three water sources ozonated. These figures are based on the information tabulated in Appendix 5.1. They indicate that in each case the removal of TOC with increasing ozone contact time (t_c) may be described by a first order system of the type:

$$\frac{d[TOC]}{dt_c} = - k_{TOC}[TOC]$$

From the slope of these curves the reaction rate constant, k_{TOC}, may be calculated and these values are recorded in Table 5.3-1. However, as noted in Section 3.3.2, the reaction of ozone with nitroaniline is mass transfer limited and thus the reaction rate constants given for this water source are considered unique to the given system and operating conditions. Run 7 using Grand River water collected during the spring snow melt appears to be best described by two first order rate processes, 7A and 7B respectively. Although the reason for this effect is unknown it is expected that the composition of this sample differs from those of the previous six runs.

While again variable, similar results were obtained for Grand River and Spencer Creek samples. The more consistent

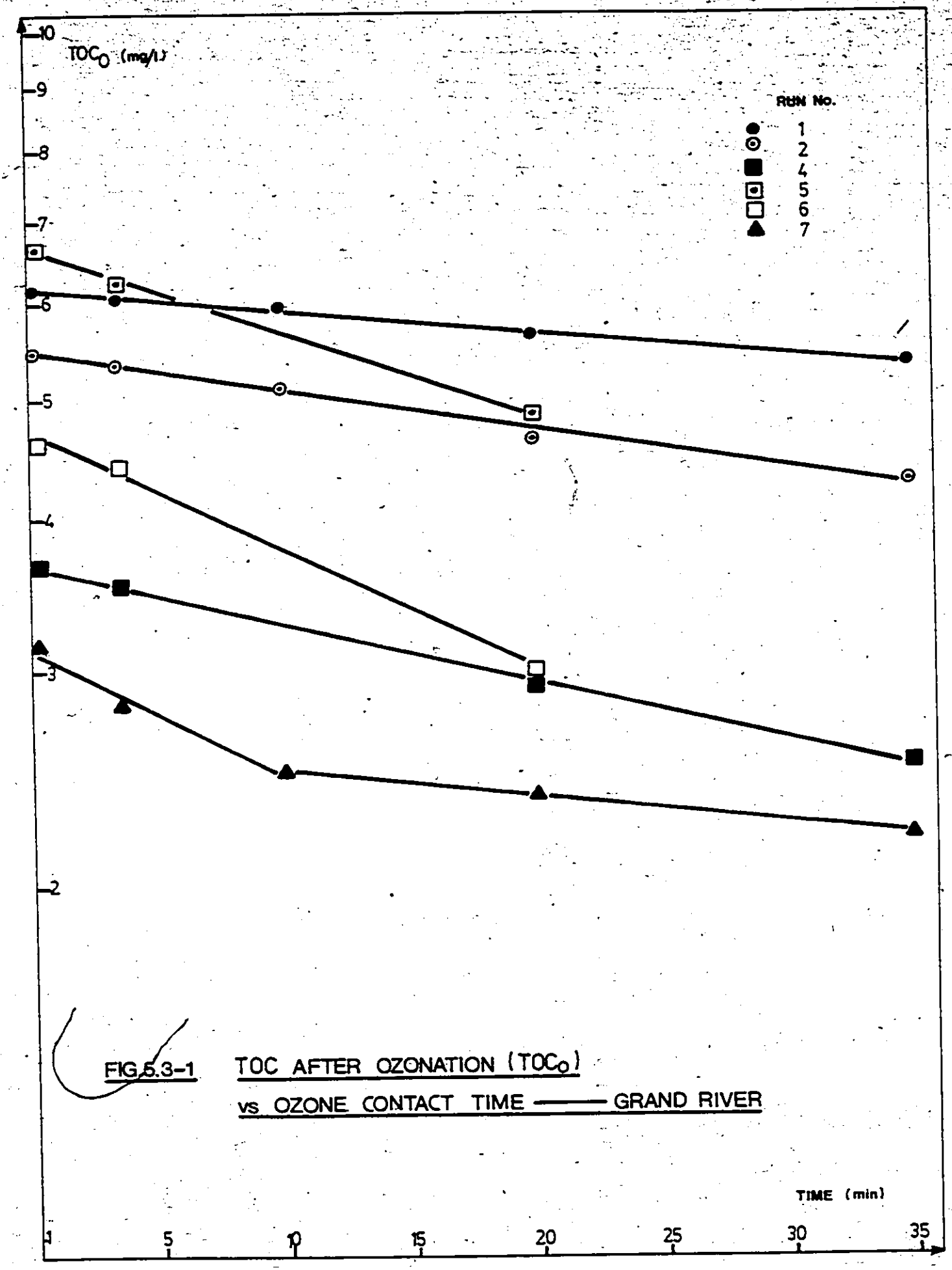


FIG.5.3-1 TOC AFTER OZONATION (TOC$_O$) vs OZONE CONTACT TIME —— GRAND RIVER

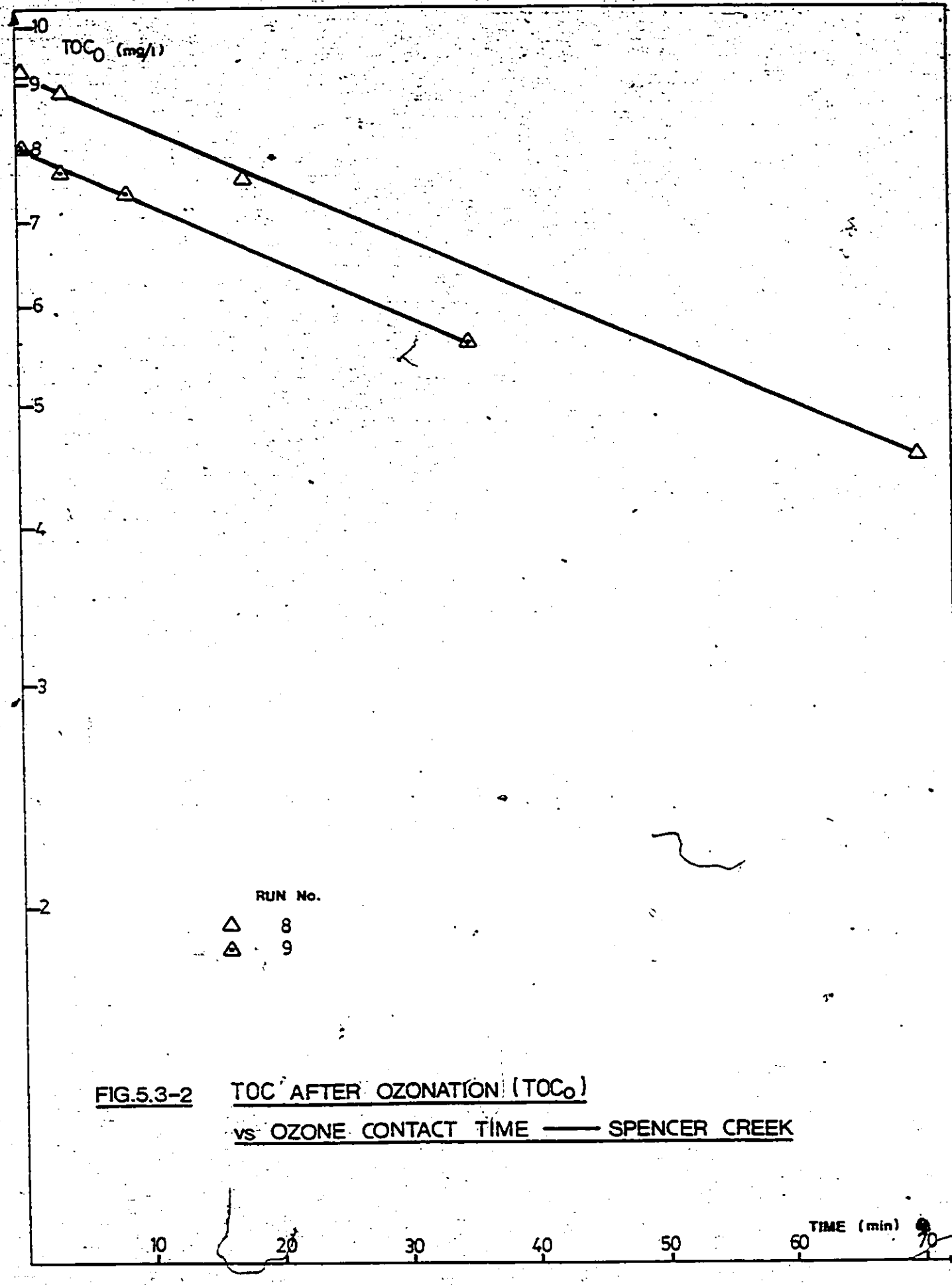


FIG.5.3-2 TOC AFTER OZONATION (TOC_o) vs OZONE CONTACT TIME —— SPENCER CREEK

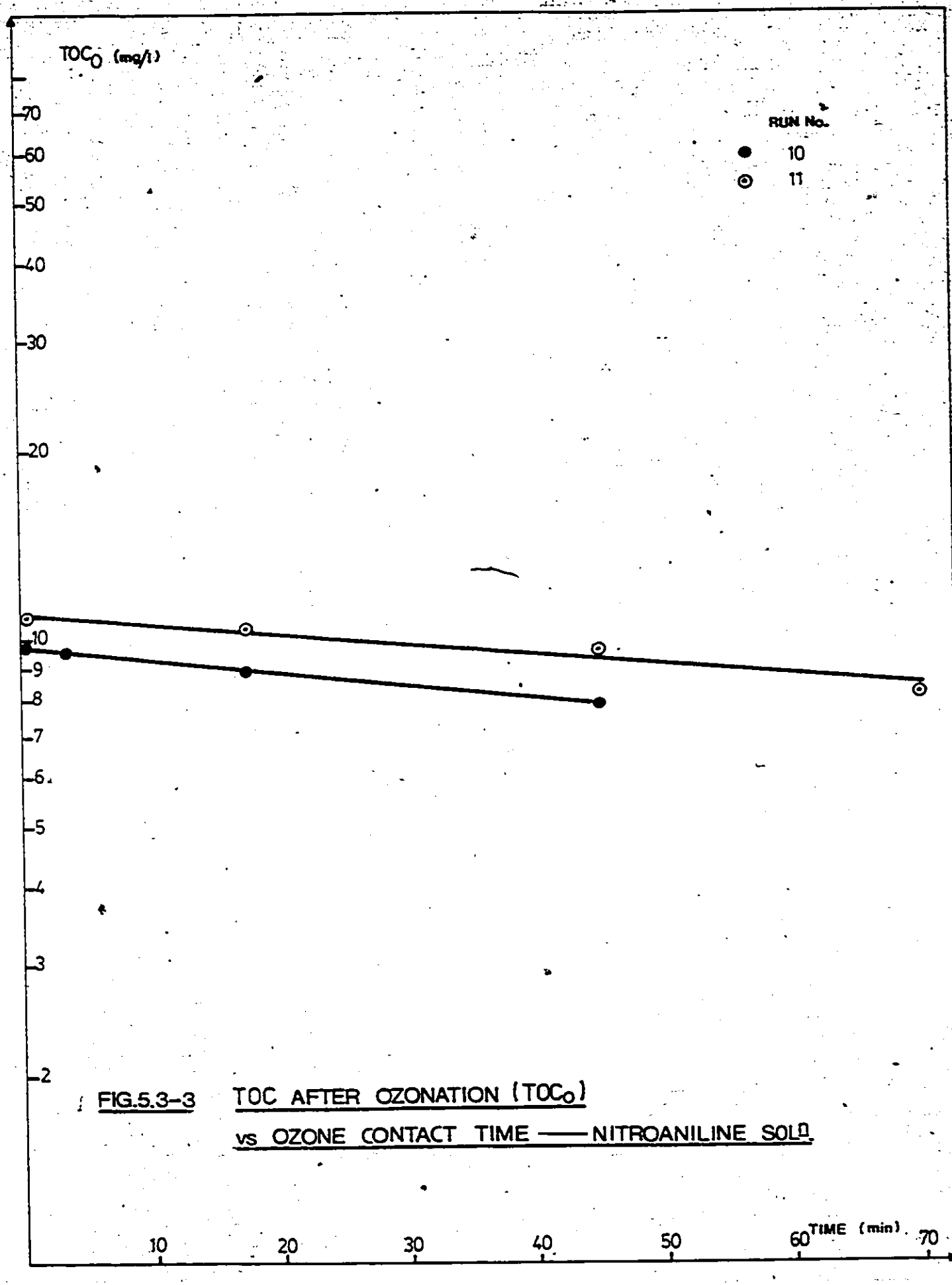


FIG.5.3-3 TOC AFTER OZONATION (TOC_O) vs OZONE CONTACT TIME —— NITROANILINE SOLN.

TABLE 5.3-1

FIRST ORDER REACTION RATE CONSTANTS (k_{TOC}) FOR TOC REMOVAL

Run No.	k_{TOC} (min^{-1})
Grand River	
1	0.0041
2	0.0073
3	-
4	0.0108
5	0.0155
6	0.0221
7 A	0.0233
B	0.0048
Spencer Creek	
8	0.0099
9	0.0102
para-Nitroaniline	
10	0.0047
ortho-Nitroaniline	
11	0.0041

values of k_{TOC} for Spencer Creek are perhaps indicative of a water source of more uniform composition. The lower values of k_{TOC} for the nitroaniline samples may in part be attributed to the earlier observation that these organics are less oxidized prior to ozonation.

First order reaction rate characteristics with respect to ozone and soluble substrate concentration have been described in the literature (Hewes & Davison, 1972; Chain et al., 1975; Hoigné & Bader, 1977). The reaction rate constants in Table 5.3-1 are of a similar magnitude to those given by Hewes and Davison (1972) for the TOC reduction of waste water effluents by ozonation.

5.3.2 TOC Reduction

For the three water sources ozonated the reduction in TOC as a function of applied ozone dose is shown in Figures 5.3-4, 5.3-5 and 5.3-6 (These figures are based on the information in Table A5.1 of Appendix 5). Grand River water data continues to emphasize the variability encountered with samples from this source. Possibly related to seasonal changes, it is considered the variable TOC removal may result from fluctuations in sample composition. This variation might be expected in a river flowing through populated and agriculturally developed areas.

Higher ozone doses favour increased TOC removal,

FIG.6.3-4 TOC REDUCTION BY OZONATION (ΔTOC_o) EXPRESSED AS A FRACTION OF THE UNOZONATED SAMPLE TOC (TOC_p) vs APPLIED OZONE DOSE GRAND RIVER

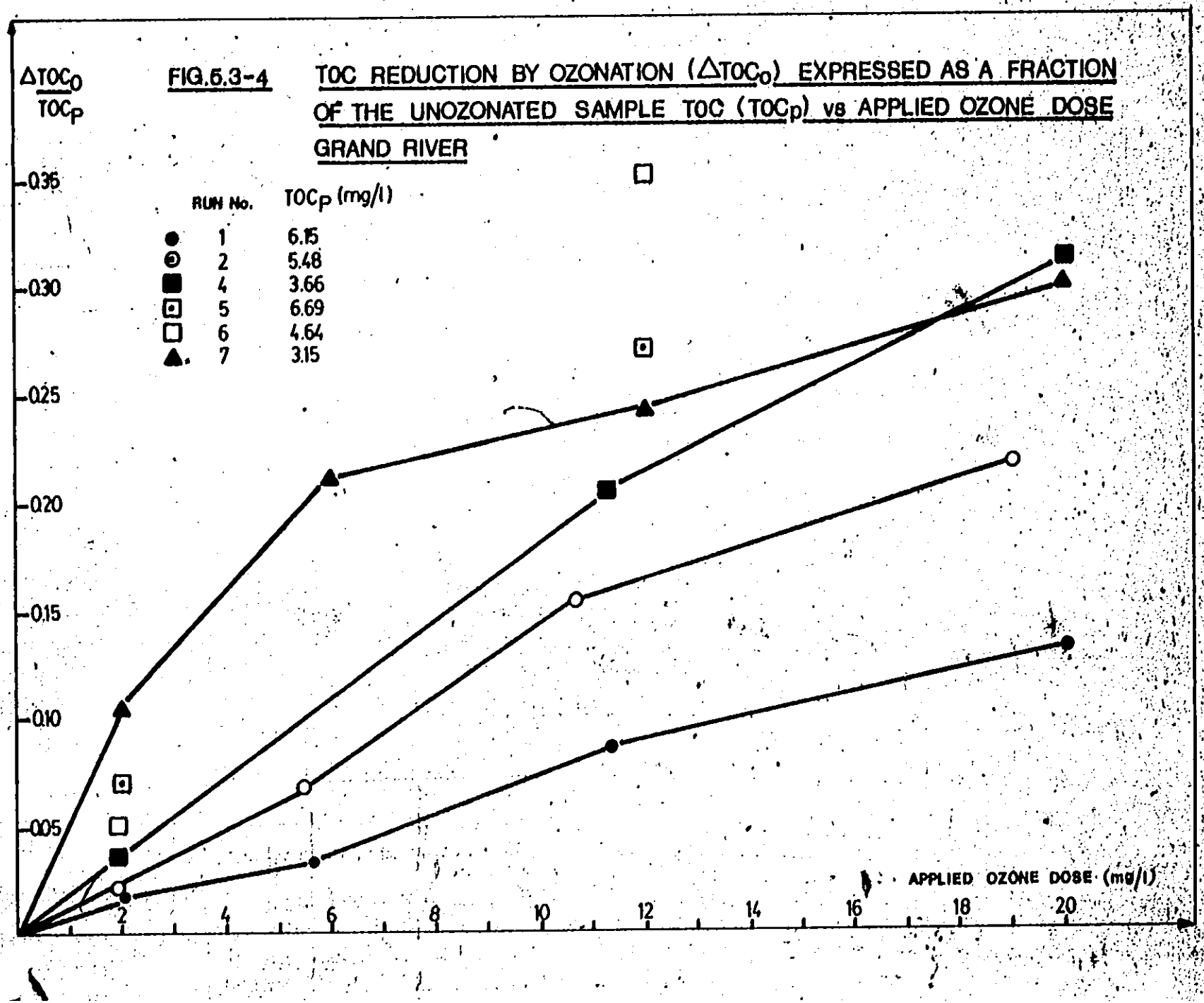


FIG.6.3-6 TOC REDUCTION BY OZONATION (ΔTOC_o) EXPRESSED AS A FRACTION OF THE UNOZONATED SAMPLE TOC (TOC_p) vs APPLIED OZONE DOSE

SPENCER CREEK

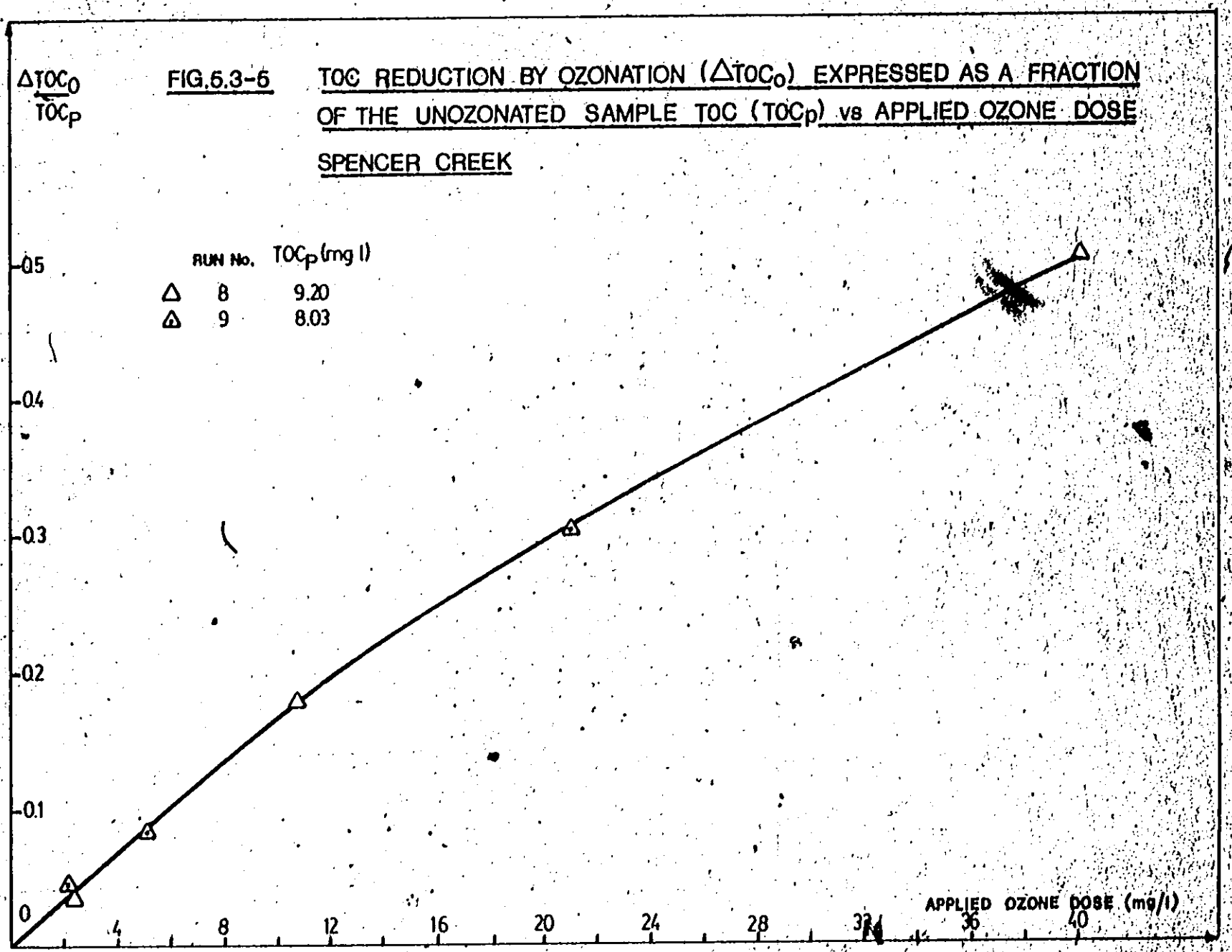
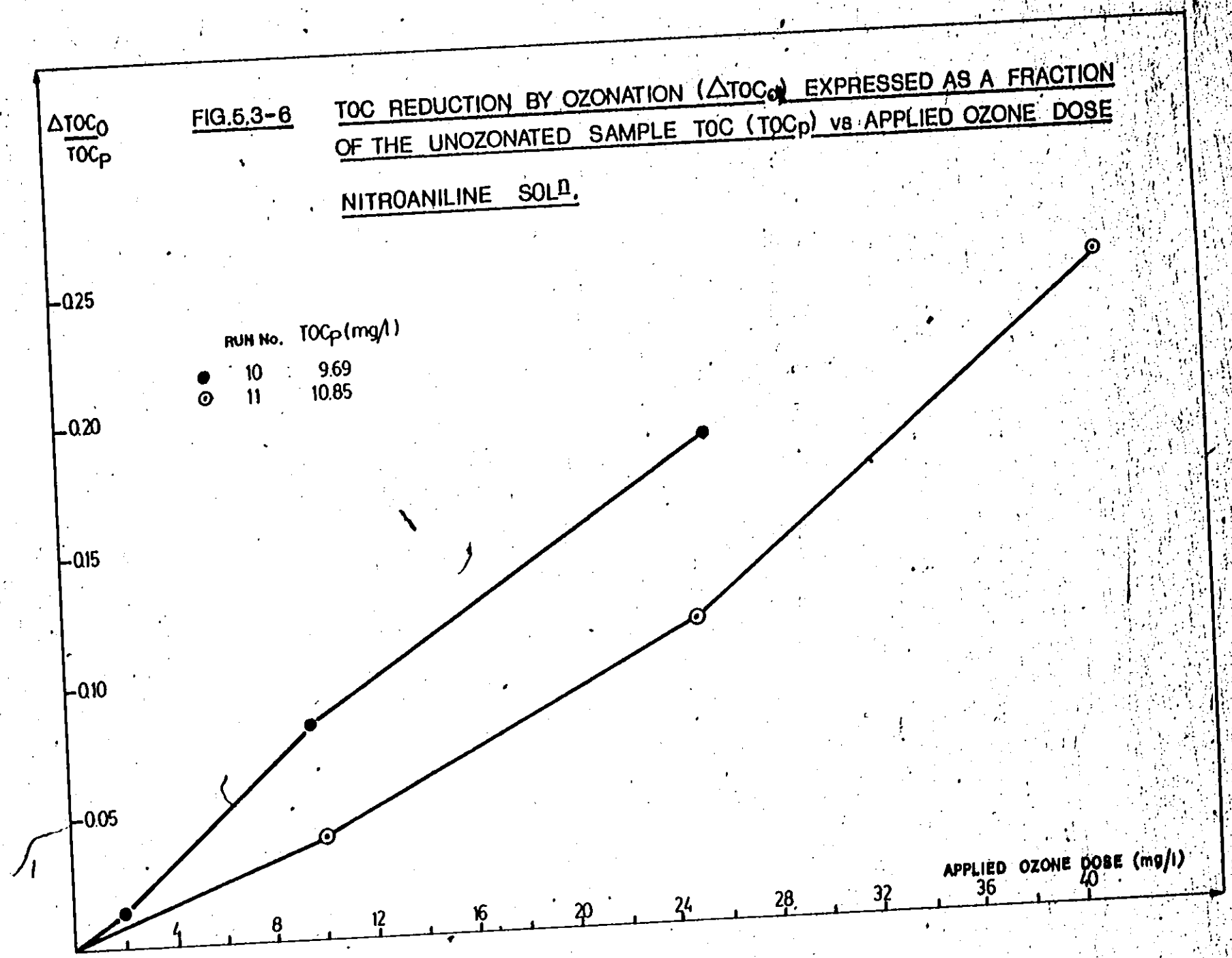


FIG.6.3-6 TOC REDUCTION BY OZONATION (ΔTOC_o) EXPRESSED AS A FRACTION OF THE UNOZONATED SAMPLE TOC (TOC_p) vs APPLIED OZONE DOSE

NITROANILINE SOL^n.



although with reduced effectiveness in terms of carbon removed for a given increase in applied ozone dose. This is consistent with the first order kinetics discussed in the previous section. By way of comparison the TOC reduction for Grand River and Spencer Creek samples was similar for similar applied ozone doses. However at the same dose TOC removal in Nitroaniline samples was approximately half that of samples from the other two sources.

As an example TOC removal from Grand River water, after an applied ozone dose of 20 mg/ℓ, ranges between 0.1-0.3 mg TOC removed per mg TOC ozonated. At ozone doses typical of water treatment plants (2-5 mg/ℓ) the expected TOC removal is 0.03-0.13 mg TOC removed per mg TOC ozonated. This data is similar to that reported by Rice et al.(1979) for ozonation practices in drinking water plants on the Rhine River where reductions range from 0.06 to 0.12 mg TOC removed per mg TOC ozonated.

5.3.3 Ozonated Sample Composition

Changes in the sample UV absorbance are partially indicative of changes in the organic composition. Absorbance measurements at a wavelength of 254 nm are proportional to the concentration of congugated carbon-carbon double bonds or aromaticity. In Figures 5.3-7, 5.3-8, and 5.3-9 the decrease in UV absorbance with increasing ozone is shown for Grand River, Spencer Creek, and Nitroaniline samples respectively.

FIG.5.3-7 FRACTION OF TOC. (TOC_0/TOC_P) AND UV ABSORBANCE (UV_0/UV_P) REMAINING AFTER OZONATION vs APPLIED OZONE DOSE

GRAND RIVER

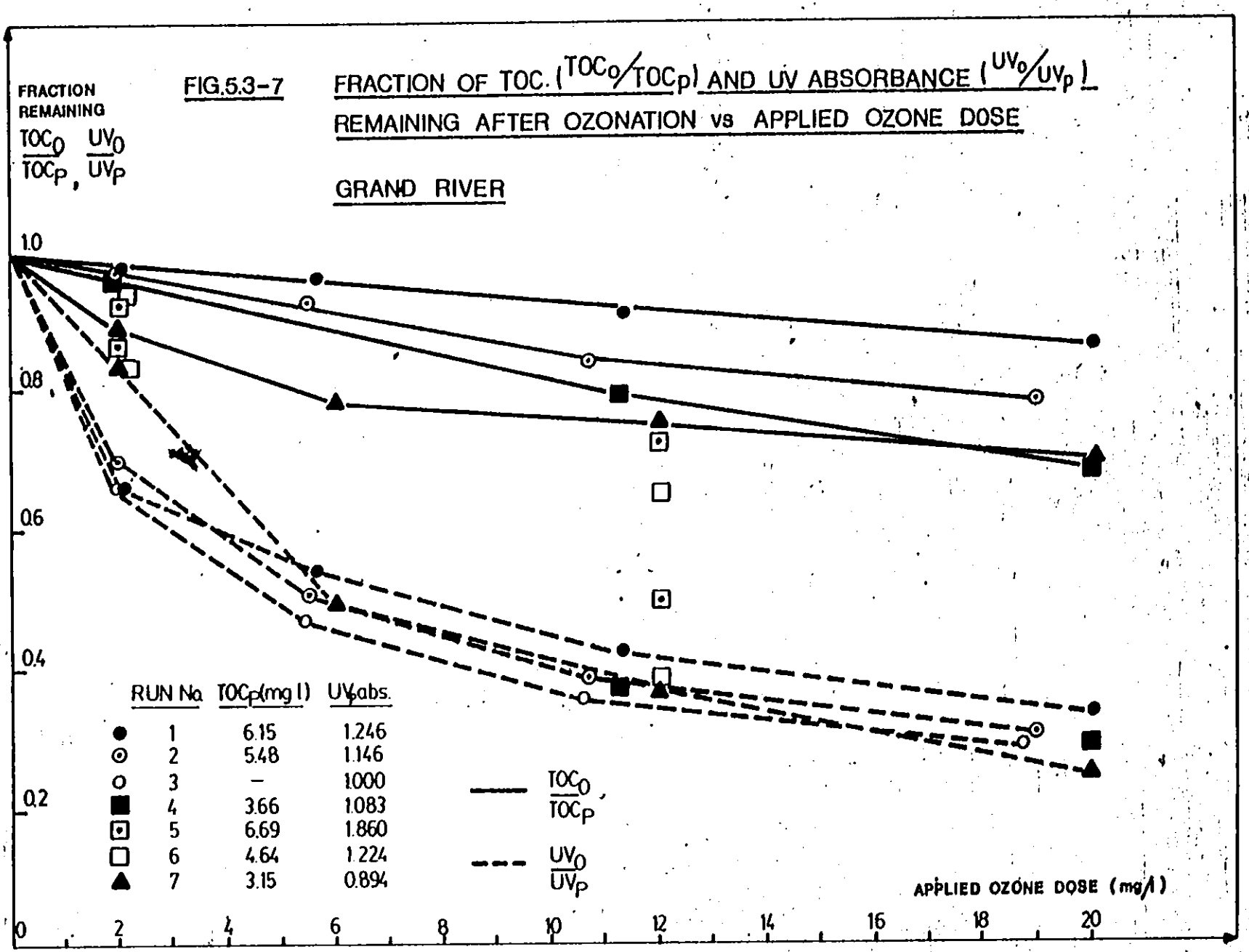


FIG.6.3-8 FRACTION OF TOC (TOC_0/TOC_p) AND UV ABSORBANCE (UV_0/UV_p) REMAINING AFTER OZONATION vs APPLIED OZONE DOSE

SPENCER CREEK

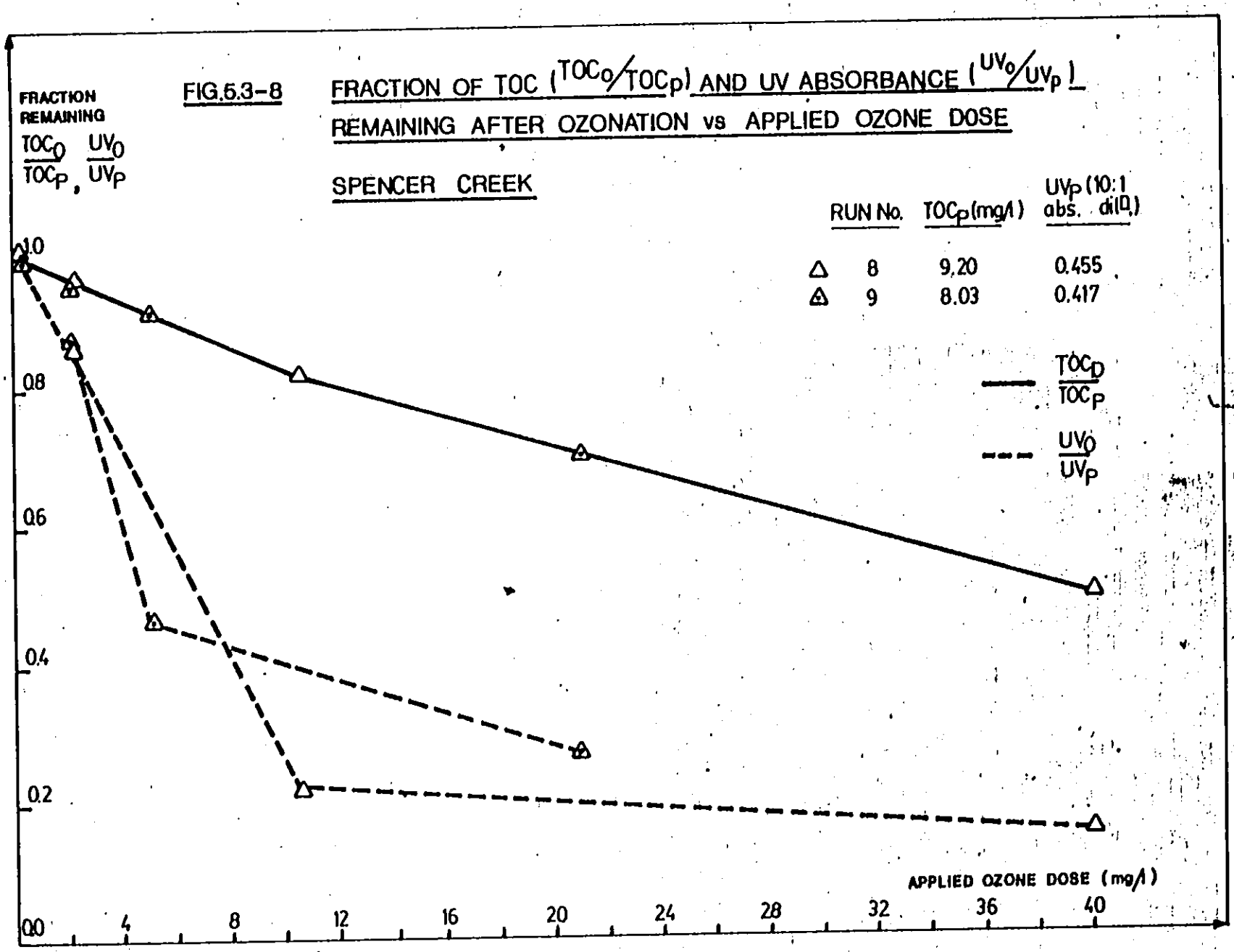
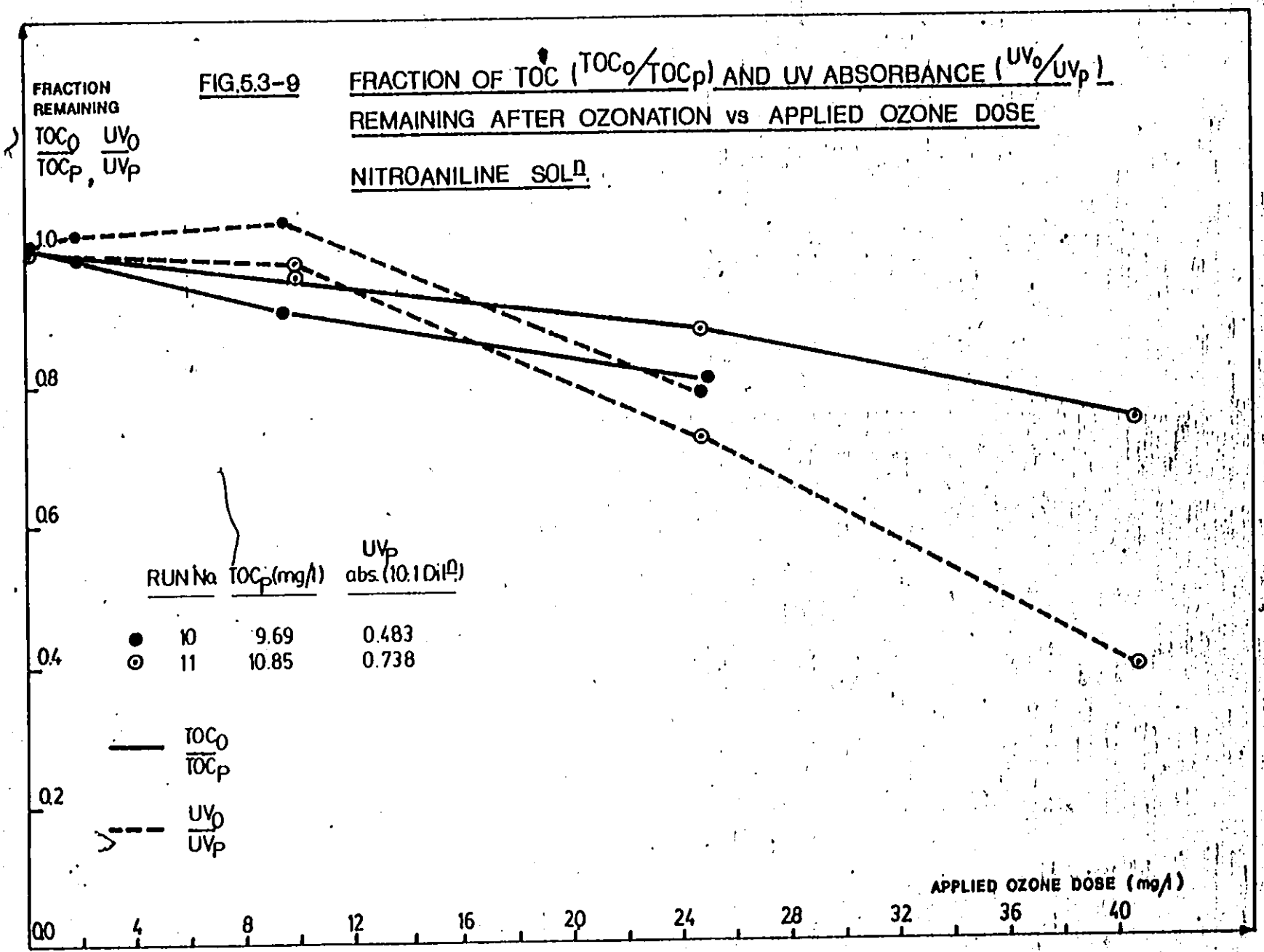


FIG.5.3-9 FRACTION OF TOC (TOC_0/TOC_P) AND UV ABSORBANCE (UV_0/UV_P) REMAINING AFTER OZONATION vs APPLIED OZONE DOSE

NITROANILINE SOLⁿ.



For comparison the TOC data is also plotted on the same basis. Reductions in the concentration of UV absorbing substances appears to be more significant than TOC reductions. This is especially evident for the ozonation of Grand River and Spencer Creek samples for which a high initial rate of decrease in UV absorbing substances was observed. It is acknowledged, however, that these conclusions are based on UV absorbance determinations at a wavelength of 254 nm only. Typically an applied ozone does of 20 mg/ℓ results in a 65-75% decrease in the concentration of UV absorbing substances while the TOC changes by only 10-30% at the same dose. In addition the UV data is more consistent, especially in the case of Grand River water.

Such rapid removals of UV absorbance were not recorded for the ozonation of nitroaniline samples at the lower ozone doses thus implying more gradual oxidation, possibly involving the oxidation of $-NH_2$ and $-NO_2$ groups in addition to the aromatic ring. As shown in Table 5.3-2 the nitrate concentration increased at higher ozone doses. Based on the concentration of nitroaniline in these samples the stoichiometric nitrate nitrogen production is 3.77 mg/ℓ and 4.22 mg/ℓ for runs 10 and 11 respectively, assuming the complete conversion of all the nitrogen present ($-NH_2$ and $-NO_2$ groups). The maximum change in the nitrate nitrogen concentration recorded in Table 5.3-2 is 2.0 mg/ℓ for the ozonation of 20.8 mg/ℓ o-Nitroaniline with 40 mg/ℓ ozone. This represents approx. 50% of the stoichiometric conversion. Further ozonation to

TABLE 5.3-2

NITRITE AND NITRATE CONCENTRATIONS FOR VARIOUS APPLIED OZONE DOSES

Water Source	Run No.	Ozone Dose (mg/ℓ)	TOC (mg/ℓ)	Nitrite (mg/ℓ as Nitrogen)	Nitrate (mg/ℓ as Nitrogen)
Grand River	4	0.0	3.66	0.00	2.23
		1.9	3.53	0.00	2.11
		11.5	2.91	0.00	2.29
		20.0	2.52	0.00	2.38
Spencer Creek	8	0.0	9.20	0.00	0.46
		2.3	8.88	0.00	0.58
		10.6	7.55	0.00	0.70
		40.0	4.57	0.00	0.80
	9	0.0	8.03	0.00	0.63
		2.1	7.67	0.00	0.68
		5.1	7.36	0.00	0.70
		20.0	5.60	0.00	0.80
para-Nitroaniline[a]	10	0.0	9.69	0.00	0.18
		1.9	9.63	0.07	0.23
		9.6	8.88	0.20	0.56
		25.6	7.88	0.12	1.35
ortho-Nitroaniline[b]	11	0.0	10.85	0.00	0.33
		10.0	10.42	0.13	0.73
		25.0	9.58	0.10	1.63
		41.2	8.11	0.04	2.32

[a,b] Stoichiometric nitrate nitrogen production is 3.77 mg/ℓ and 4.22 mg/ℓ respectively.

doses of 40 mg/ℓ produced more significant decreases in UV absorbance, most likely resulting from the rupture of the aromatic ring. An ozone dose of 40 mg/ℓ corresponds to approximately 6 moles of ozone per mole of nitroaniline. As discussed in the literature (Section 2.4.4) 4-6 moles of ozone per mole of phenol is sufficient to rupture the aromatic ring. This data is further supported by the work of Glabisz and Tomaszewska (1977) who found ozone simultaneously attacks the amino and nitro groups and the aromatic ring. They also observed small quantities of brown intermediate products formed at the lower ozone doses. Glabisz and Tomaszewska attributed this to the formation of quinonian type compounds. Other oxidation products included unsaturated dicarboxylic acids, maleic and formic acids.

It is postulated that decreased aromaticity, as evidenced by a reduction in UV absorbance, may result in the formation of more biodegradable products like those discussed in Section 2.4.4.

5.4 PARTIAL OXIDATION OF ORGANICS

5.4.1 Effect of Ozonation on $\frac{COD}{TOC}$ Ratio

Ozonation results in reduced COD/TOC ratios for samples from each water source. This effect is shown in Figures 5.4-1, 5.4-2 and 5.4-3 based on the data listed in Table A5.1 in Appendix 5. Hence the relative reduction in COD is greater than that of TOC for a specific ozone dose. Thus it is concluded that all, or a part of, those organics remaining are more oxidized than the original substances. The effect is most pronounced for the ozonation of nitro-aniline solutions where an applied ozone dose of 4 mg O_3/mg TOC reduced the COD/TOC ratio in excess of 50%. Corresponding changes for Grand River and Spencer Creek samples were 25-40% and 10-20% respectively.

5.4.2 Partially Oxidized Organic Fraction Remaining after Ozonation

It has been established in Section 5.4.1 that in addition to the complete oxidation of TOC to carbon dioxide during ozonation a proportion of the remaining organics are oxidized, but not completely to carbon dioxide. Based on the change in sample COD and TOC a parameter (f) may be defined to specify the extent of partial oxidation. The overall change in COD (ΔCOD_o) due to ozonation provides the total sample oxidation while the proportion of this accounted for by complete oxidation

FIG.6.4-1 COD/TOC RATIO AFTER OZONATION (COD_o/TOC_o) vs APPLIED OZONE DOSE PER UNIT INITIAL TOC (TOC_p)

GRAND RIVER

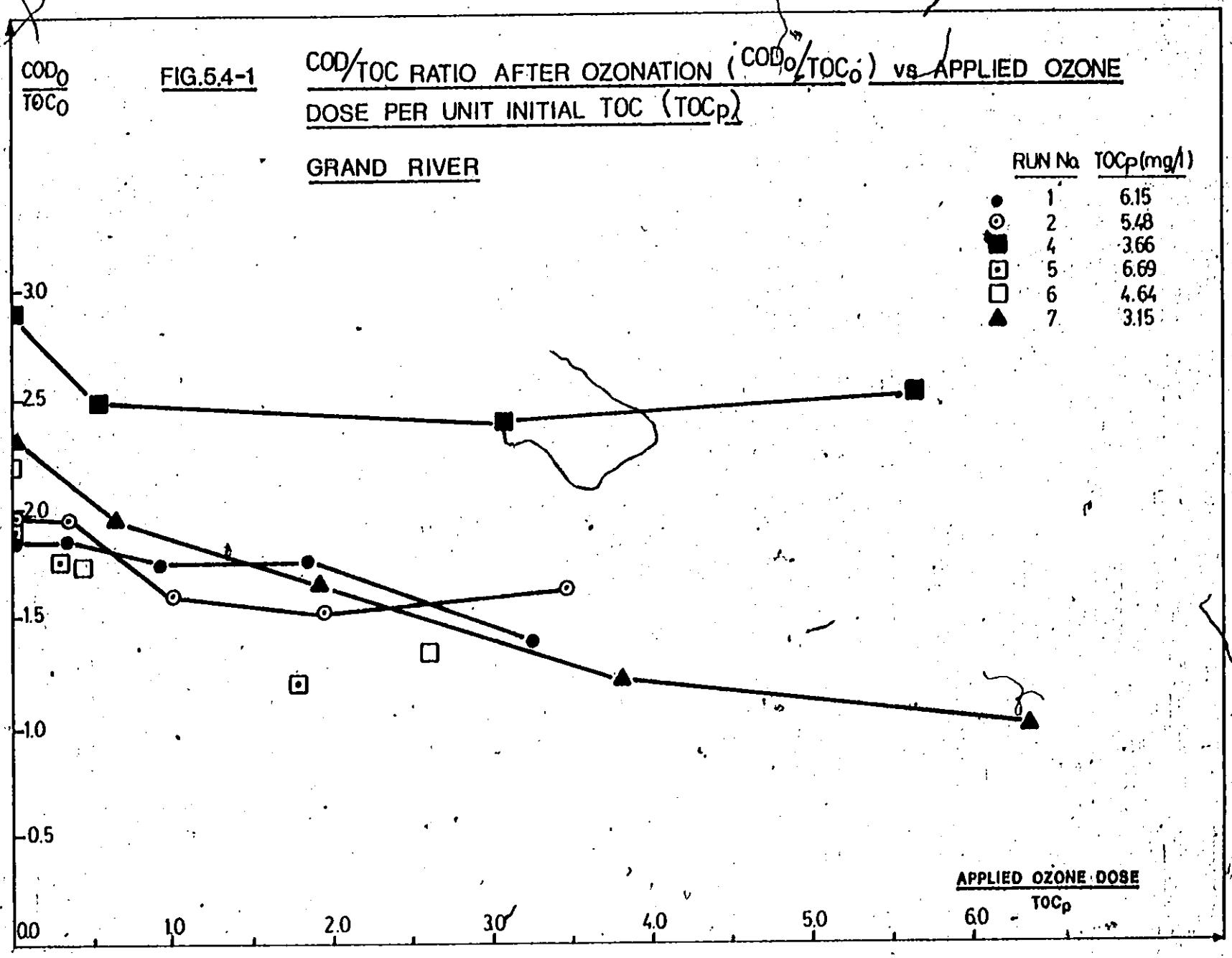


FIG.5.4-2 COD/TOC RATIO AFTER OZONATION (COD_o/TOC_o) vs APPLIED OZONE DOSE PER UNIT INITIAL TOC (TOC_p)

SPENCER CREEK

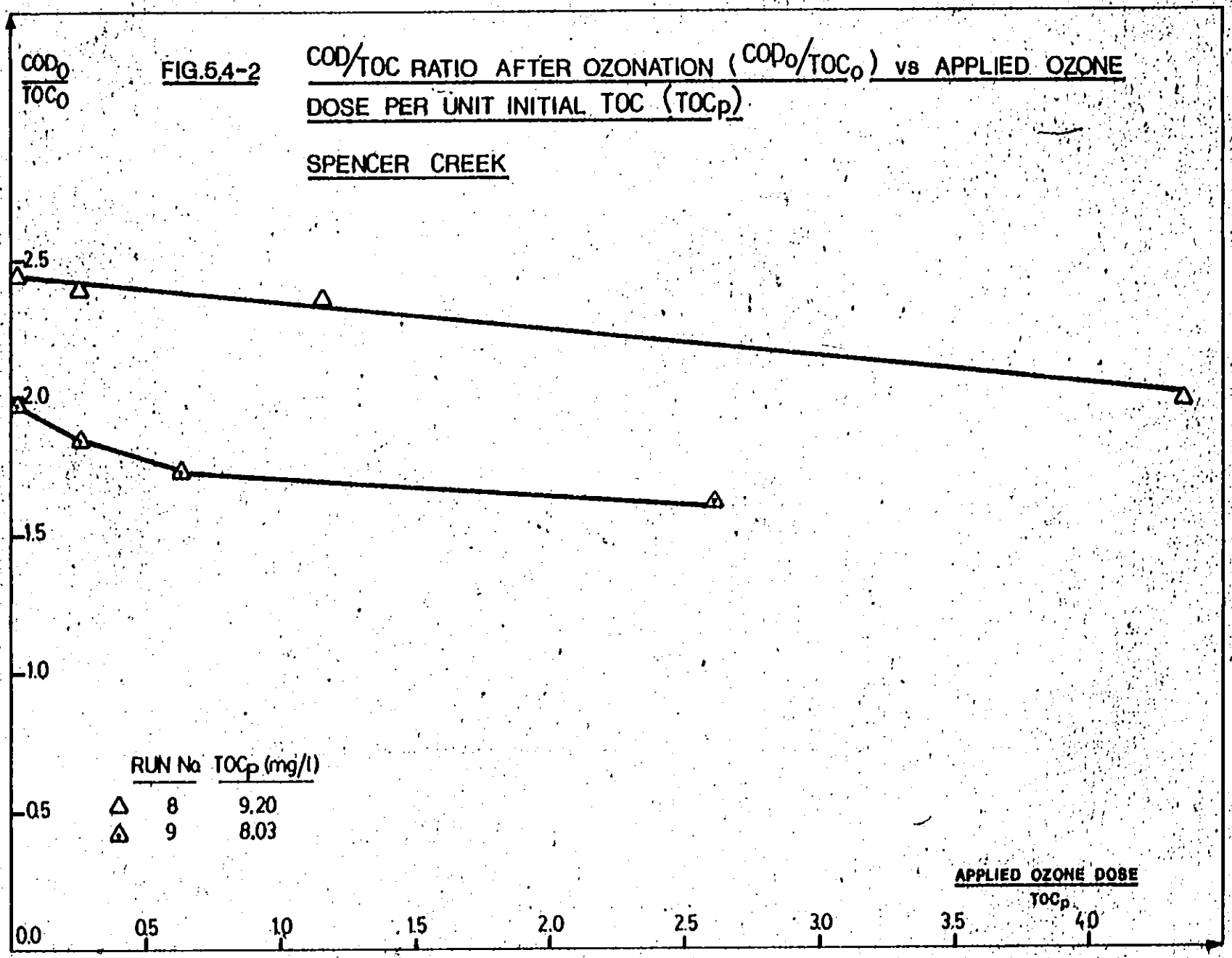
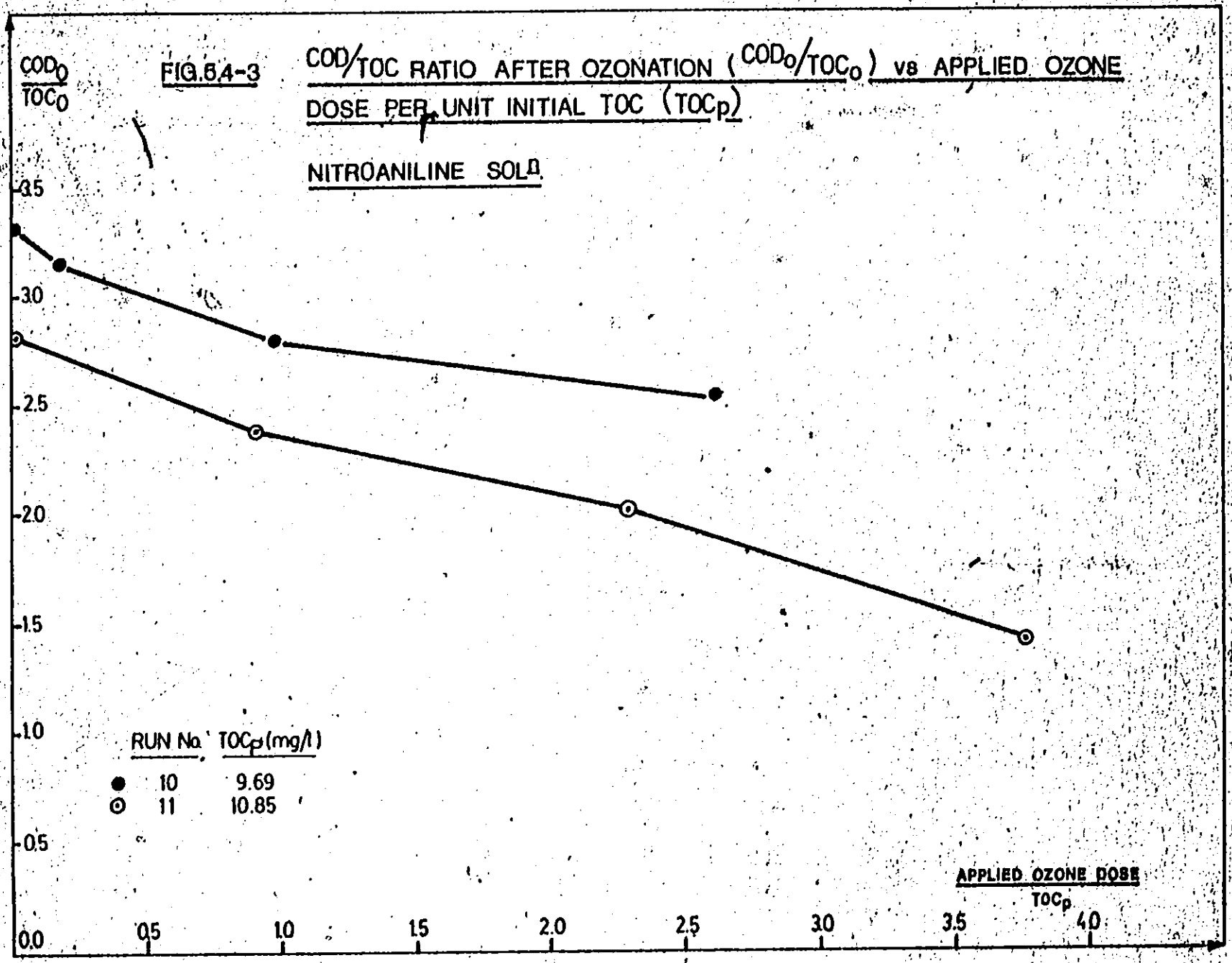


FIG.6.4-3 COD/TOC RATIO AFTER OZONATION (COD_o/TOC_o) vs APPLIED OZONE DOSE PER UNIT INITIAL TOC (TOC_p)

NITROANILINE SOLⁿ.



to carbon dioxide may be calculated from the change in TOC (ΔTOC_o). The parameter, f, is thus defined as follows:

$$f = \frac{\Delta COD_o - X \cdot \Delta TOC_o}{COD_o} \qquad (5.4\text{-}1)$$

where, COD_o The sample Chemical Oxygen Demand after ozonation.

X A constant expressing TOC removal as an equivalent reduction in Chemical Oxygen Demand. The value of this constant is specific to a particular water source and has been estimated as 2.62 for Grand River and Spencer Creek water, and as 3.33 for aqueous nitroaniline solutions. Refer to Appendix 5.2 for calculation details.

Then on the basis of equation (5.4-1) and the data recorded in Table A5.1 in Appendix 5, the values of f have been calculated for Grand River, Spencer Creek, and Nitroaniline samples and plotted as a function of applied ozone dose per unit initial COD (COD_p) in Figures 5.4-4, 5.4-5 and 5.4-6 respectively. The intepretation of the Grand River and Spencer Creek results is difficult. Considerable variability is evident, which is a reflection of both experimental error and the enhancement of this error in the calculation of f by equation (5.4-1). Conclusions based on the Nitroaniline data are considered valid due to the more positive changes in TOC and COD recorded and the more consistent data. In general the following trends may be observed:

FIG.6-4-4 PARTIALLY OXIDIZED ORGANIC FRACTION, f VS APPLIED OZONE DOSE PER UNIT INITIAL COD (COD_p)

GRAND RIVER

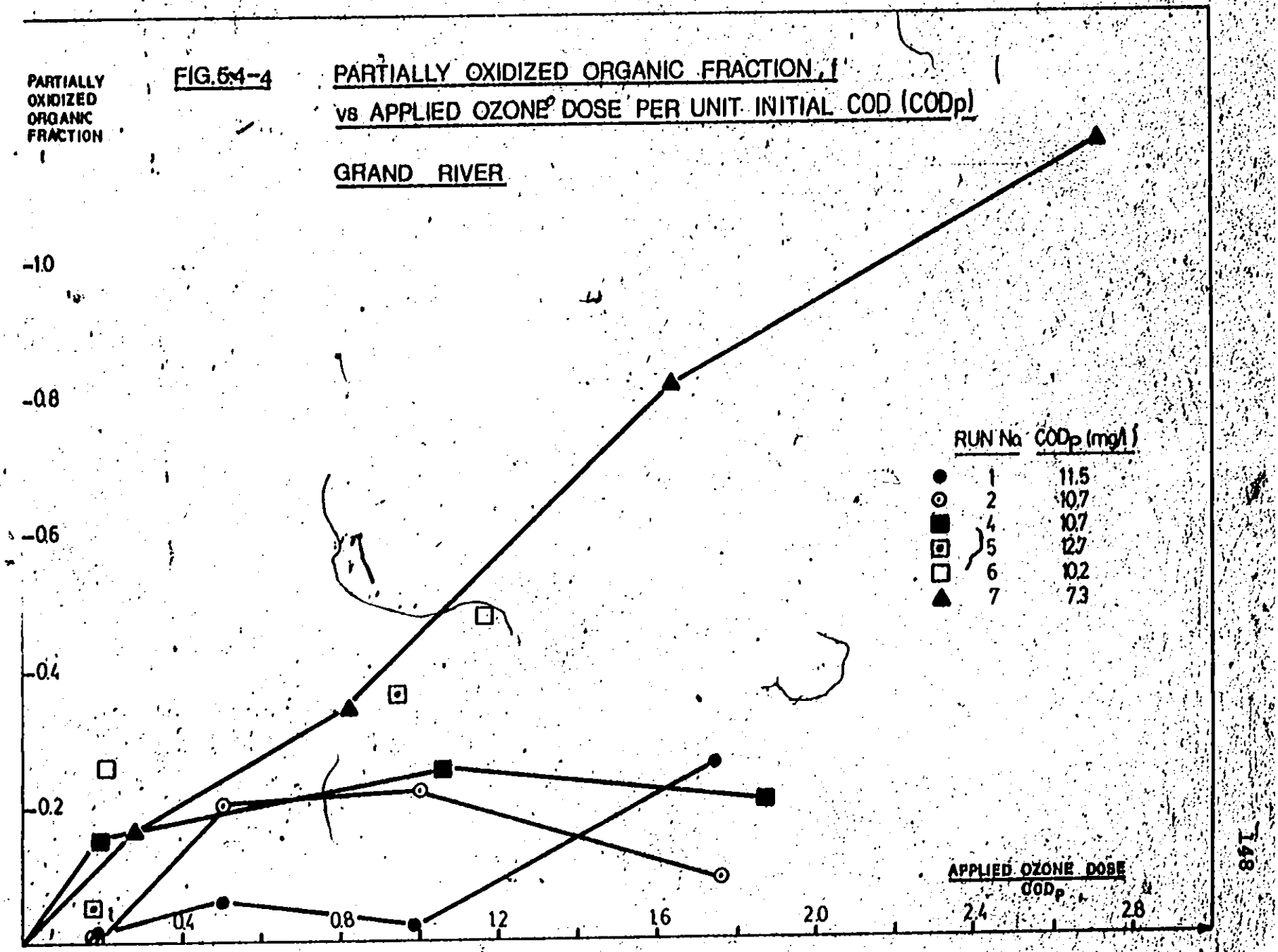


FIG. 5.4-5 PARTIALLY OXIDIZED ORGANIC FRACTION, f VS APPLIED OZONE DOSE PER UNIT INITIAL COD (CODp)

SPENCER CREEK

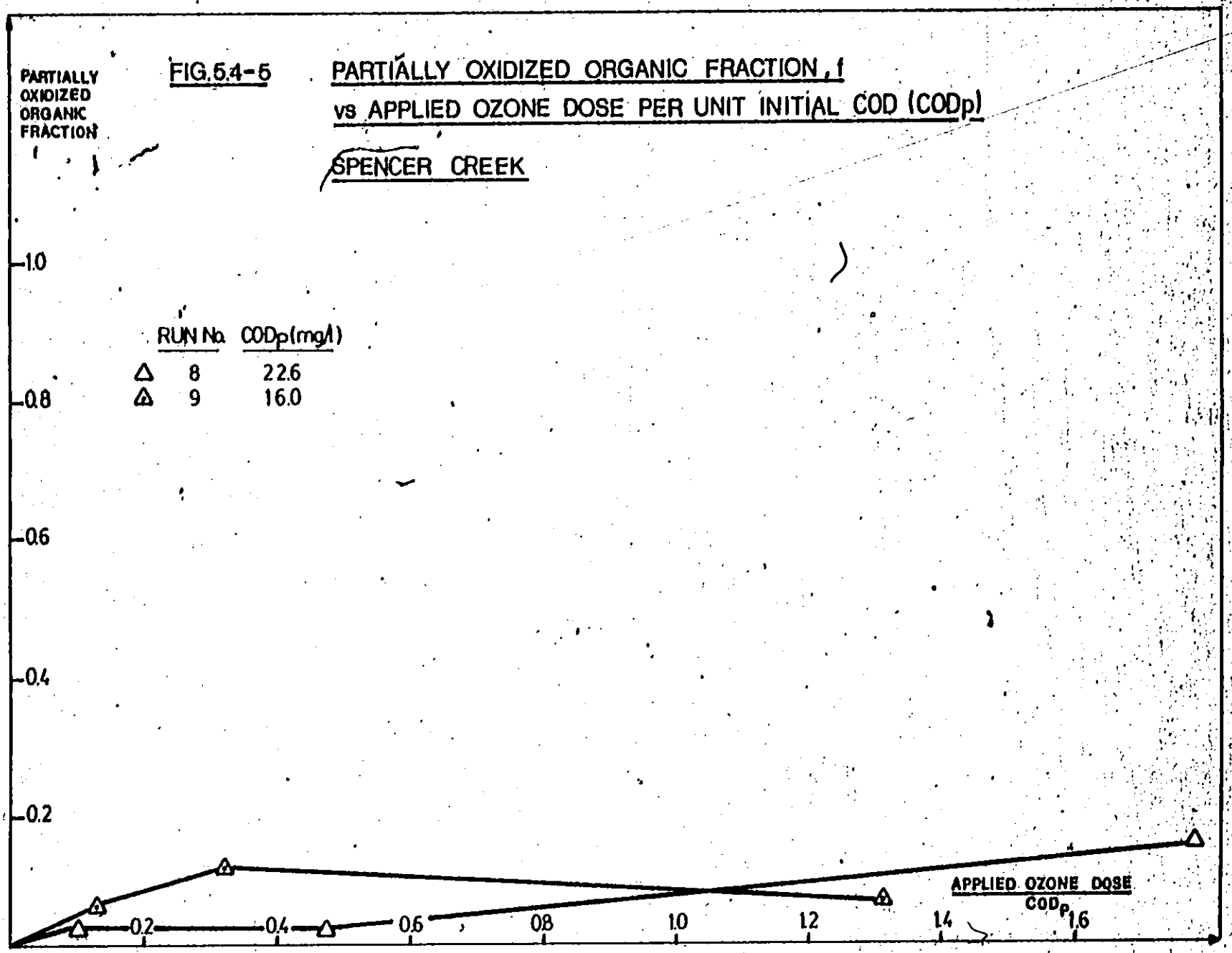
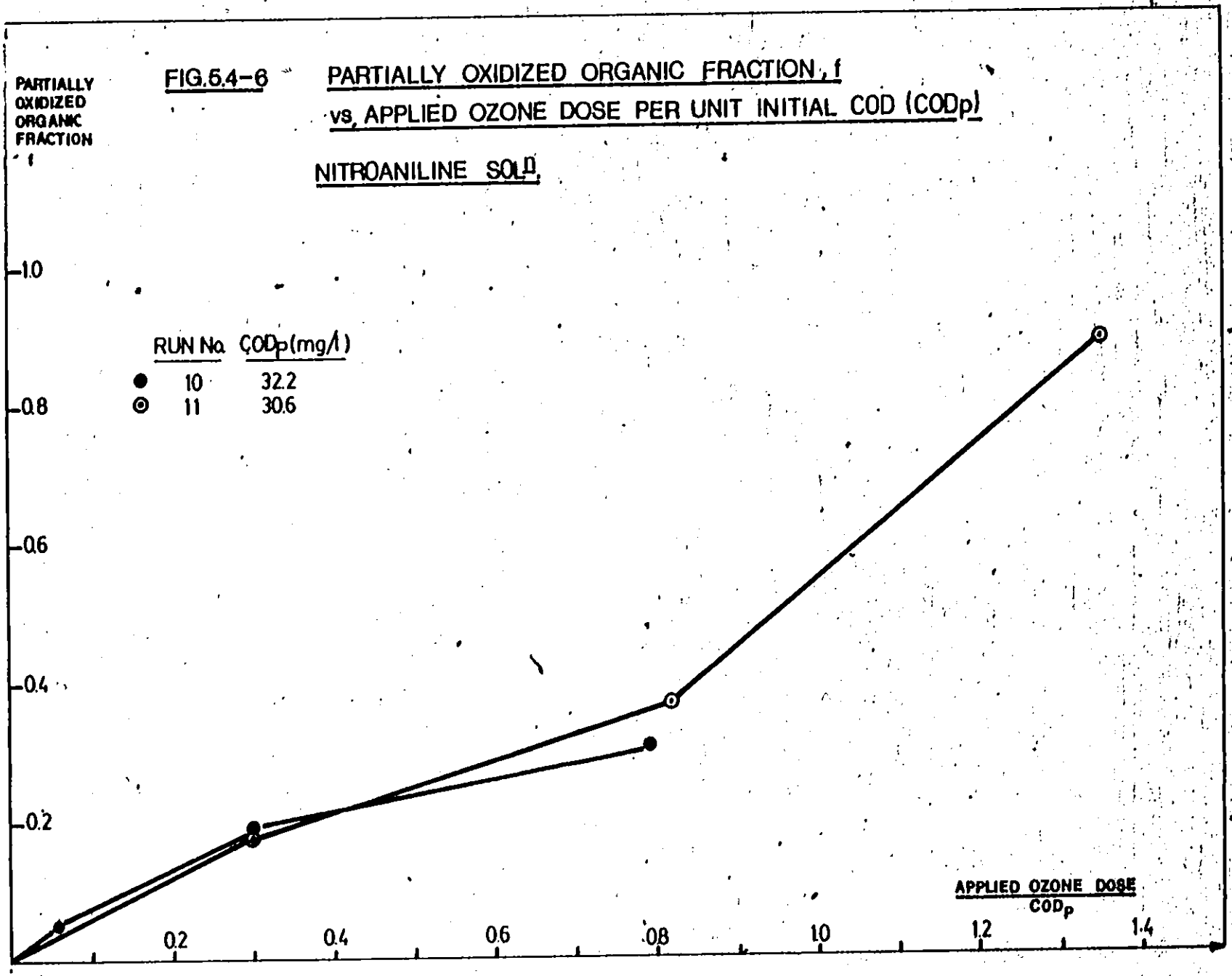


FIG.6.4-6 PARTIALLY OXIDIZED ORGANIC FRACTION, f VS. APPLIED OZONE DOSE PER UNIT INITIAL COD (COD_p)

NITROANILINE SOLN.



(i) The oxidized fraction f is increased by ozonation. For Grand River and Spencer Creek samples, however, limiting values of f appear to be approximately 0.2 and 0.1 respectively.

(ii) For a given ozone dose per unit initial COD the resulting oxidized fraction f, is highest for Nitroaniline samples, and lowest for those from Spencer Creek. This is consistent with previous conclusions pertaining to changes in the COD/TOC ratio.

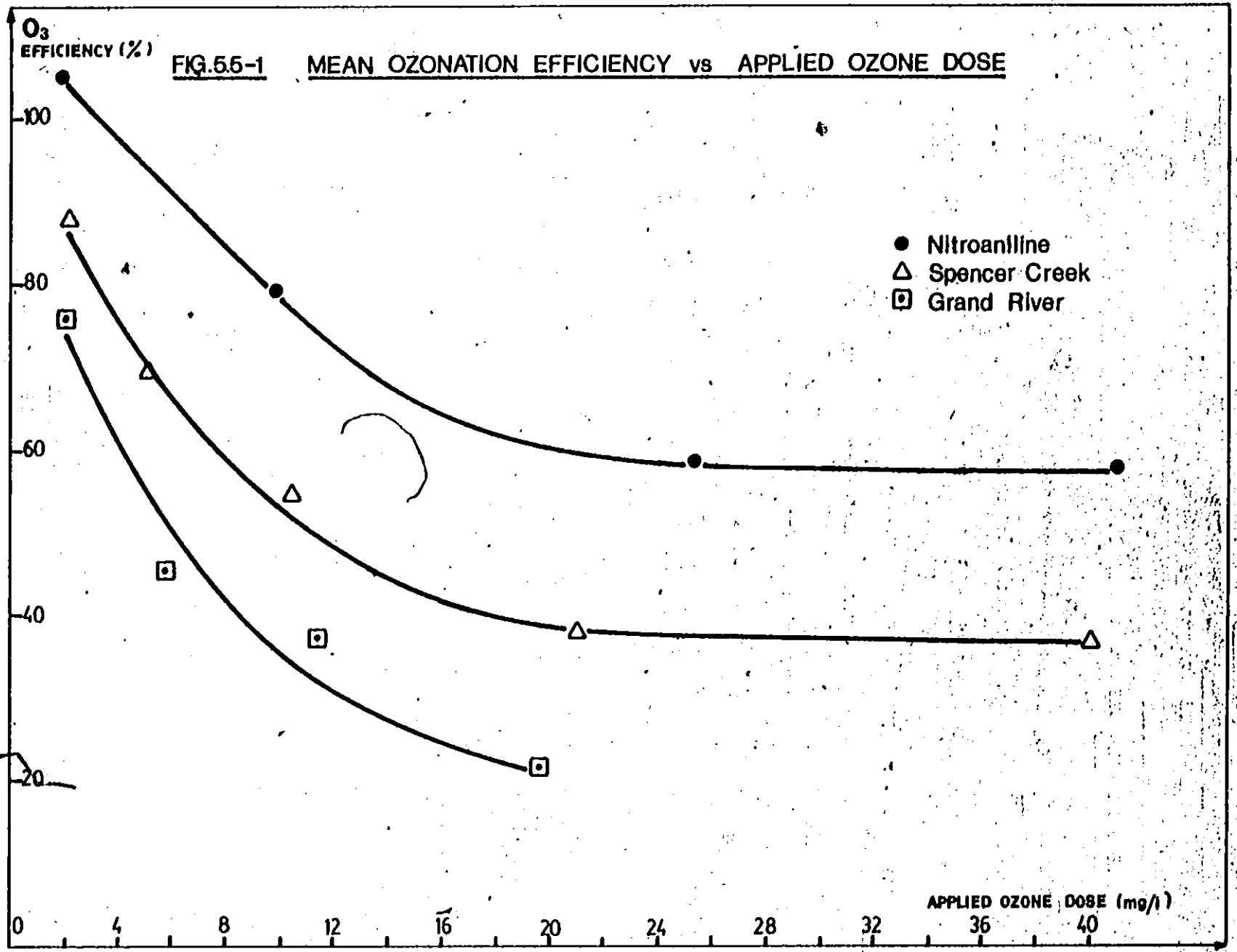
5.5 OZONATION EFFICIENCY

Ozonation Efficiency, ξ, as defined by equation 5.5-1 below, is based on the change in total oxygen demand for a specific applied ozone dose (O_3). The total oxygen demand incorporates the change in Chemical Oxygen Demand (ΔCOD_o) and the change in Nitrogen Oxygen Demand (ΔNOD_o) after ozonation. Consideration is given to the NOD as this is not measured in the COD test. Based on the proposed mechanism for 1-3 dipolar cyclo addition of ozone to unsaturated carbon bonds (as shown in Figures 2.4-2 and 2.4-3) it is assumed all three oxygen atoms in the ozone molecule may be effective for oxidation.

$$\xi = \frac{\Delta COD_o + \Delta NOD_o}{O_3} \qquad (5.5\text{-}1)$$

Ozonation efficiencies have been calculated for each water source as a function of applied ozone dose. The results are tabulated in Table A5.3, Appendix 5, and the mean data shown graphically in Figure 5.5-1. Ozonation efficiency decreases with increasing ozone dose. Efficiencies in excess of 100% are explained by the reaction of additional oxygen directly from the air stream (Huibers et al., 1969). COD ozonation efficiencies for Nitroaniline samples were significantly higher than other samples for the same ozone dose. This trend is to be expected after previously noting nitroaniline samples were more extensively oxidized by ozone.

FIG.5.5-1 MEAN OZONATION EFFICIENCY vs APPLIED OZONE DOSE



SECTION 6

BIODEGRADATION

6.1 OXYGEN UPTAKE

6.1.1 Glucose Calibration

To check the equipment and experimental procedure two Biochemical Oxygen Demand (BOD) determinations were carried out using 100 mg/ℓ glucose, a substrate of known BOD_5. Nutrient salts were added in the same proportion as those specified in Standard Methods (1975) and 100 mls of filtered activated sludge effluent was used as an inoculum. The oxygen uptake curves obtained are shown in Figure 6.1-1. The shape of the curves and the height of the plateau agree with the results of Busch (1958). The BOD_5 of 0.72 g O_2/g glucose compares favourably with that of 0.75 given in Standard Methods (1975).

6.1.2 Inoculum Acclimation

For the Grand River and Spencer Creek biodegradation experiments freshly prepared inoculum from activated sludge effluent was used. Acclimation was judged to be unnecessary in view of the diverse bacterial species present in this inoculum being considered similar to those found in surface waters.

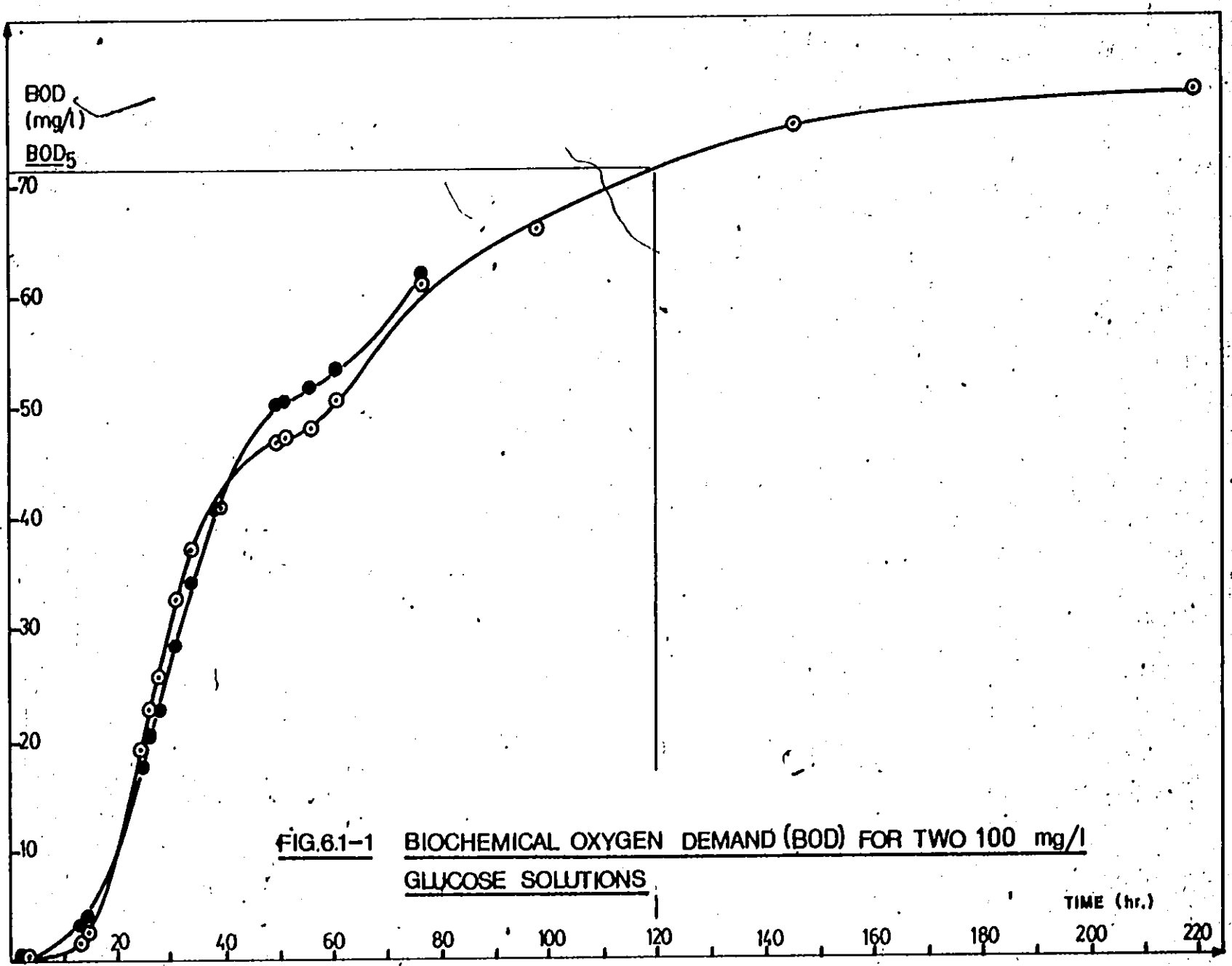


FIG.6.1-1 BIOCHEMICAL OXYGEN DEMAND (BOD) FOR TWO 100 mg/l GLUCOSE SOLUTIONS

Inoculum for the Nitroaniline studies was prepared in laboratory 6 ℓ batch activated sludge reactors. These were operated on a draw and fill basis, being fed daily with 3 ℓ raw sewage, 50 mg/ℓ glucose, 200 mg/ℓ ethanol and 10 mg/ℓ of the particular nitroaniline isomer. In this manner a vigorous growth of bacteria was maintained in the reactors for three weeks prior to extracting an inoculum for the appropriate biodegradation experiments. Bacterial activity was evaluated on the basis of TOC analyses and the concentration of nitroaniline isomer qualitatively determined from absorbance measurements. An absorbance maximum was observed at 380 nm for a 10 mg/ℓ sample of para-Nitroaniline using a Beckman (Beckman Instruments Inc., Rollerton, Georgia, U.S.A.) Spanning Spectrophotometer.

Typically TOC was reduced from 130-160 mg/ℓ to 10-15 mg/ℓ over a 24-hour period. The inoculum was extracted at the end of a cycle to minimize TOC addition to the respirometers. In Figure 6.1-2 the absorbance is plotted as a function of acclimation time for the two nitroaniline isomers. The sharp decrease in absorbance for para-nitroaniline after 6 days implies this substrate is relatively easily biodegraded. As shown this is not the case for ortho-nitroaniline for which no evidence of biodegradation was observed.

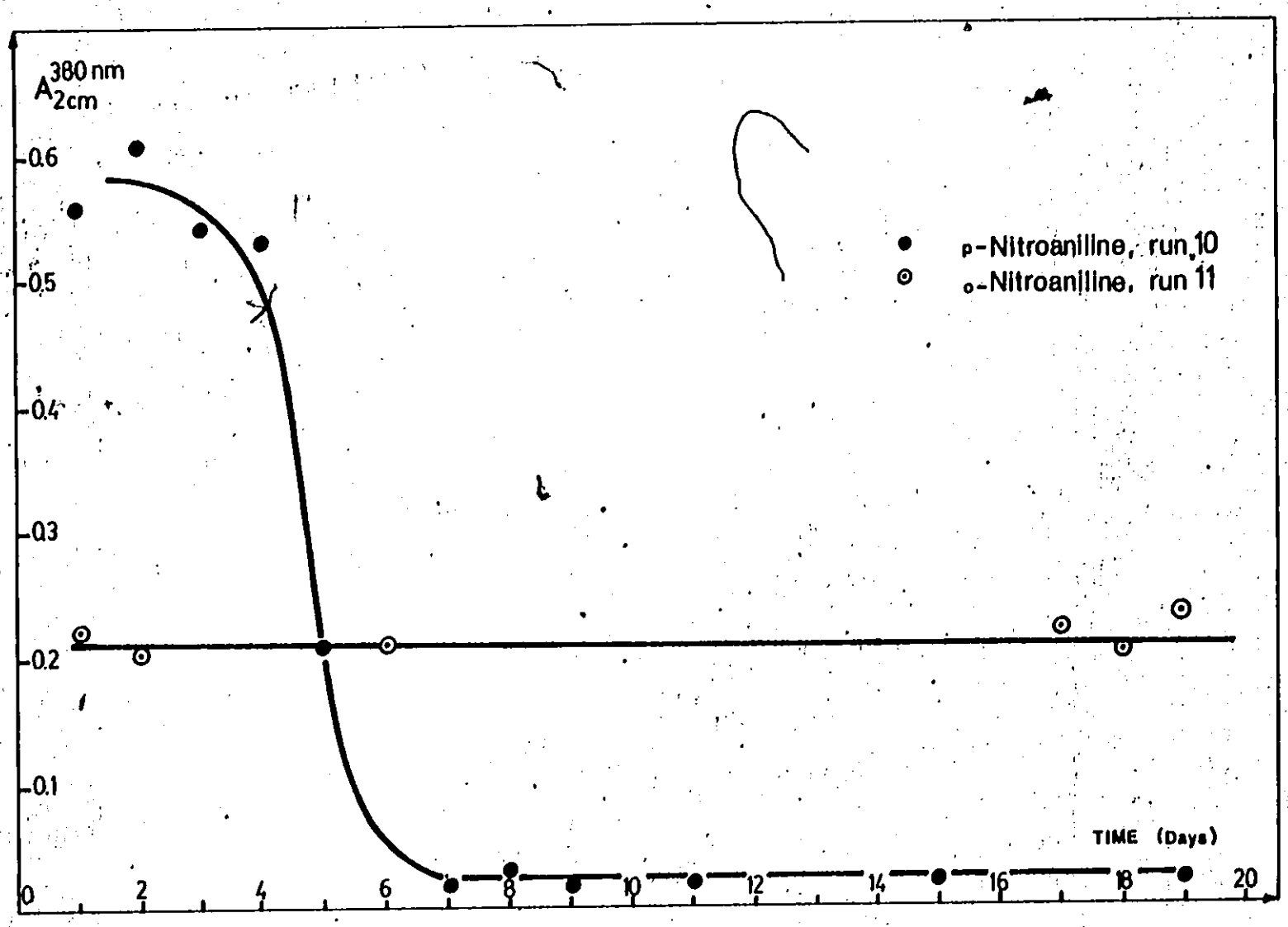


FIG. 6.1-2 ABSORBANCE (A^{380nm}_{2cm}) OF FILTERED BATCH REACTOR EFFLUENT vs ACCLIMATION TIME (samples diluted 6:1)

6.1.3 Oxygen Uptake

The Biochemical Oxygen uptakes recorded after ozonation of the various substrates at specific levels are shown in Figures 6.1-3, 6.1-4, 6.1-5 and 6.1-6. These graphs are based on the tables in Section A6.1 of Appendix 6. Grand River (Fig. 6.1-3) and Spencer Creek (Fig. 6.1-4) results are expressed in terms of the difference between oxygen uptake after ozonation (OU_{OB}) and the oxygen uptake of an unozonated sample (OU_B). The oxygen uptake of unozonated samples was essentially zero for the first 10 days incubation. Beyond this time nitrification in a number of samples resulted in significant oxygen uptake. Nitrite and nitrate concentrations before and after biodegradation are shown in Table A8.1 in Appendix 8 for some runs. Total oxygen uptake results indicate the following:

(i) Oxygen uptake increased after ozonation implying that ozonated by-products are more biodegradable than the original substrate.

(ii) After sufficient incubation a plateau like region is reached in most instances indicating the point of micro-organism food limitation. The values for these are shown in Table A6.3 in Appendix 6, and summarized in Figure 6.1-7.

FIG.6.1-3 MEAN DIFFERENCE IN CUMULATIVE OXYGEN UPTAKE (OU) BETWEEN THE OZONATED (OU_{OB}) AND THE UNOZONATED (OU_B) SAMPLES FOR VARIOUS APPLIED OZONE DOSES vs INCUBATION TIME

GRAND RIVER (Mean of runs 3,4,5,6,7)

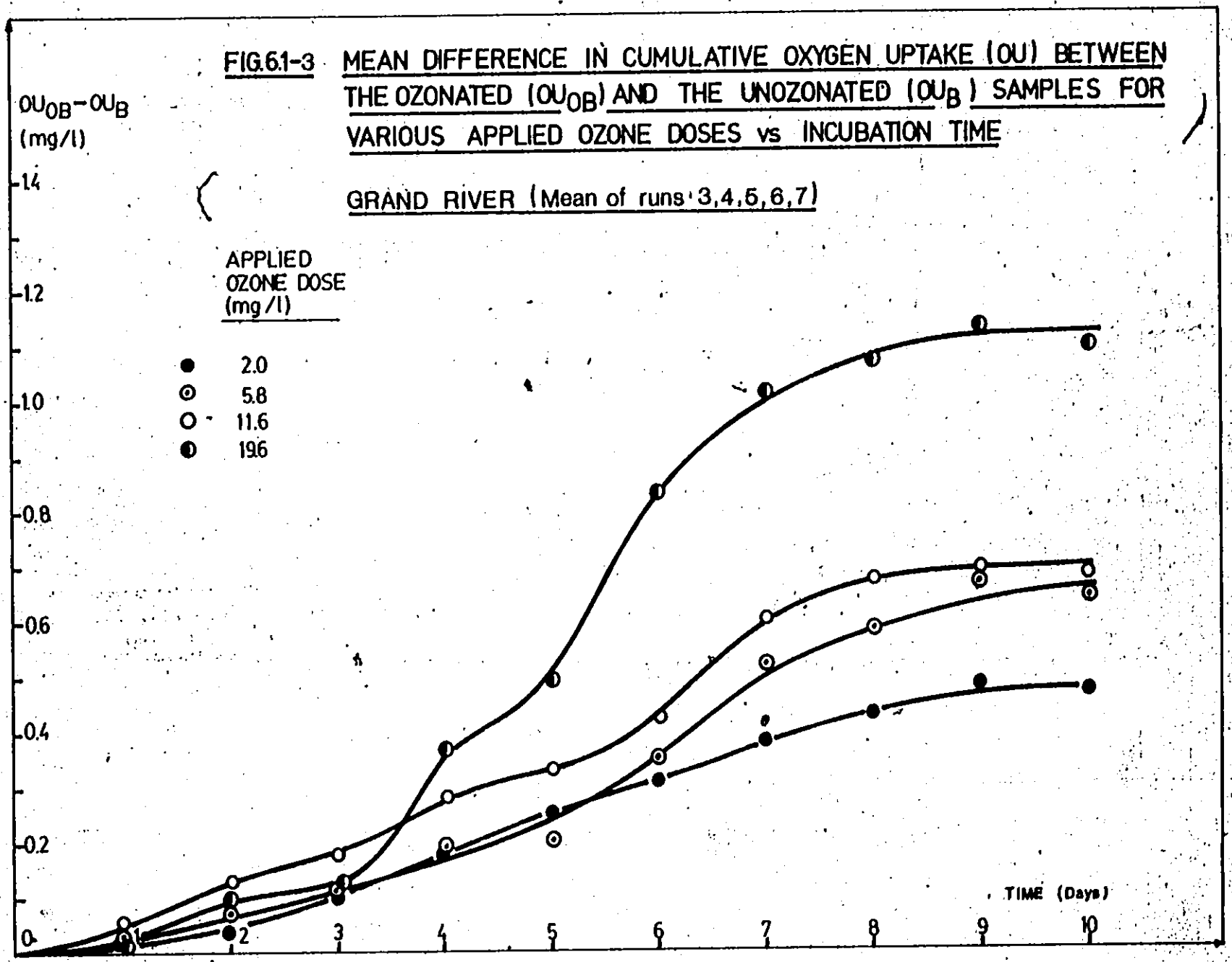
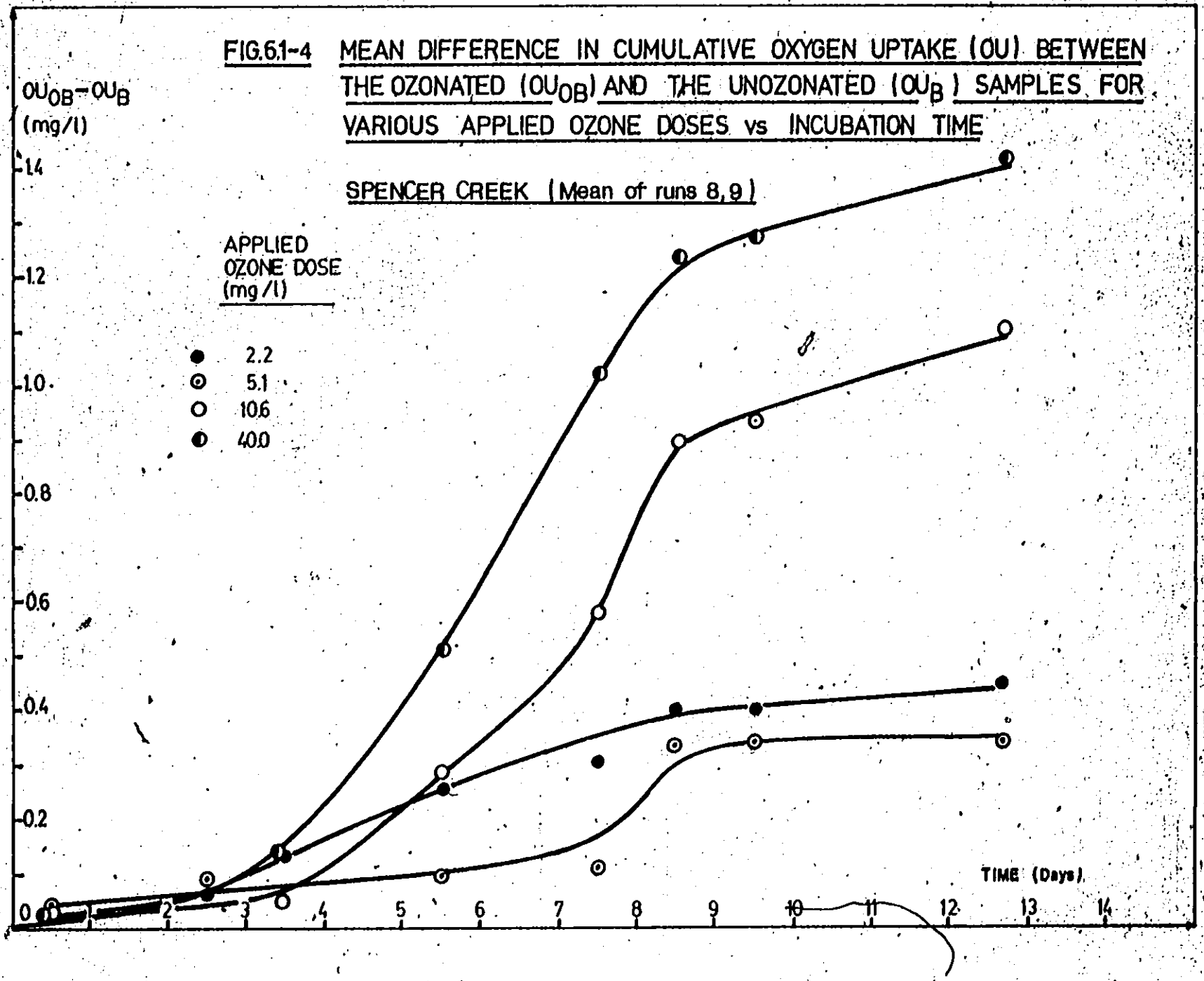


FIG.6.1-4 MEAN DIFFERENCE IN CUMULATIVE OXYGEN UPTAKE (OU) BETWEEN THE OZONATED (OU_{OB}) AND THE UNOZONATED (OU_B) SAMPLES FOR VARIOUS APPLIED OZONE DOSES vs INCUBATION TIME

SPENCER CREEK (Mean of runs 8,9)



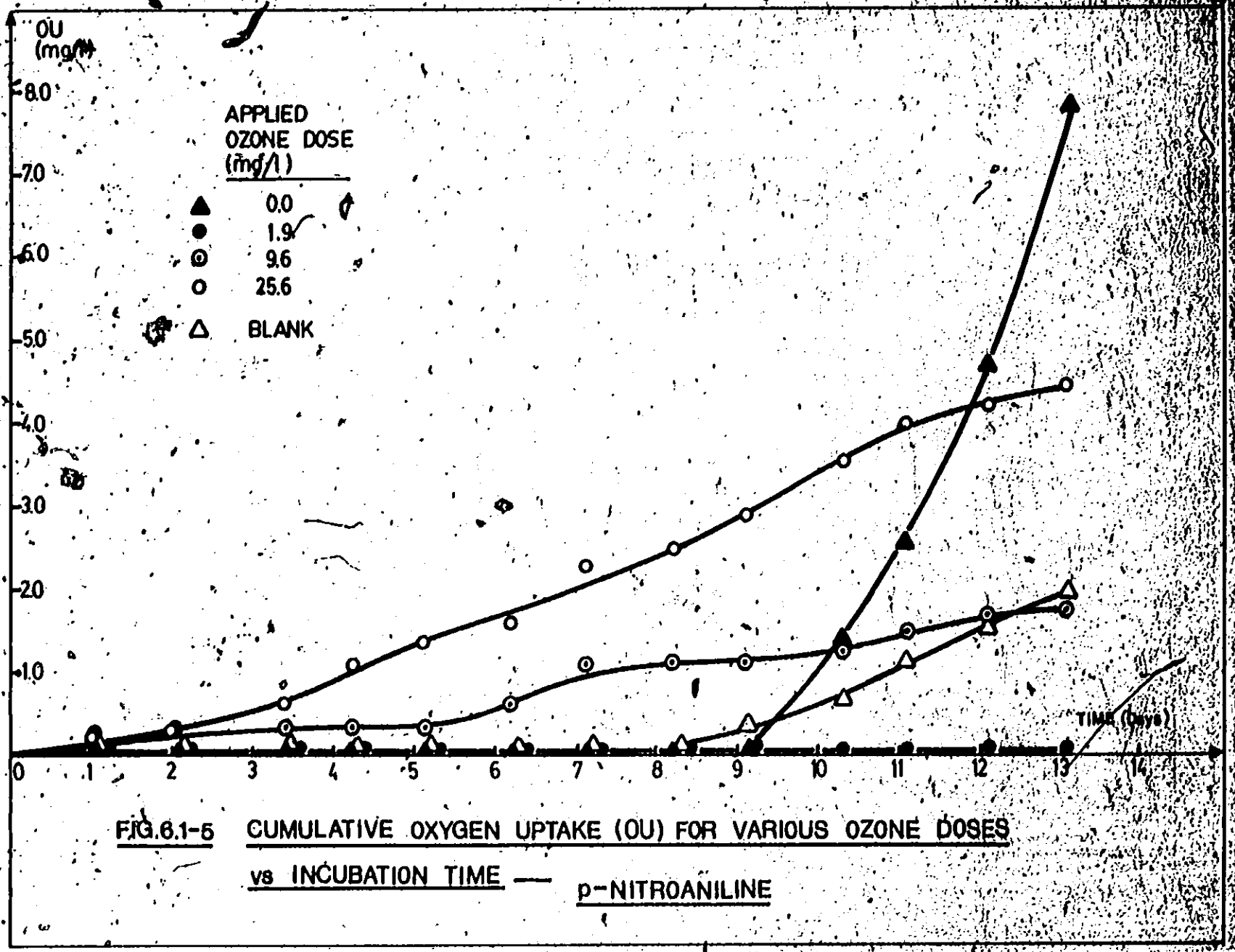


FIG.6.1-5 CUMULATIVE OXYGEN UPTAKE (OU) FOR VARIOUS OZONE DOSES vs INCUBATION TIME — p-NITROANILINE

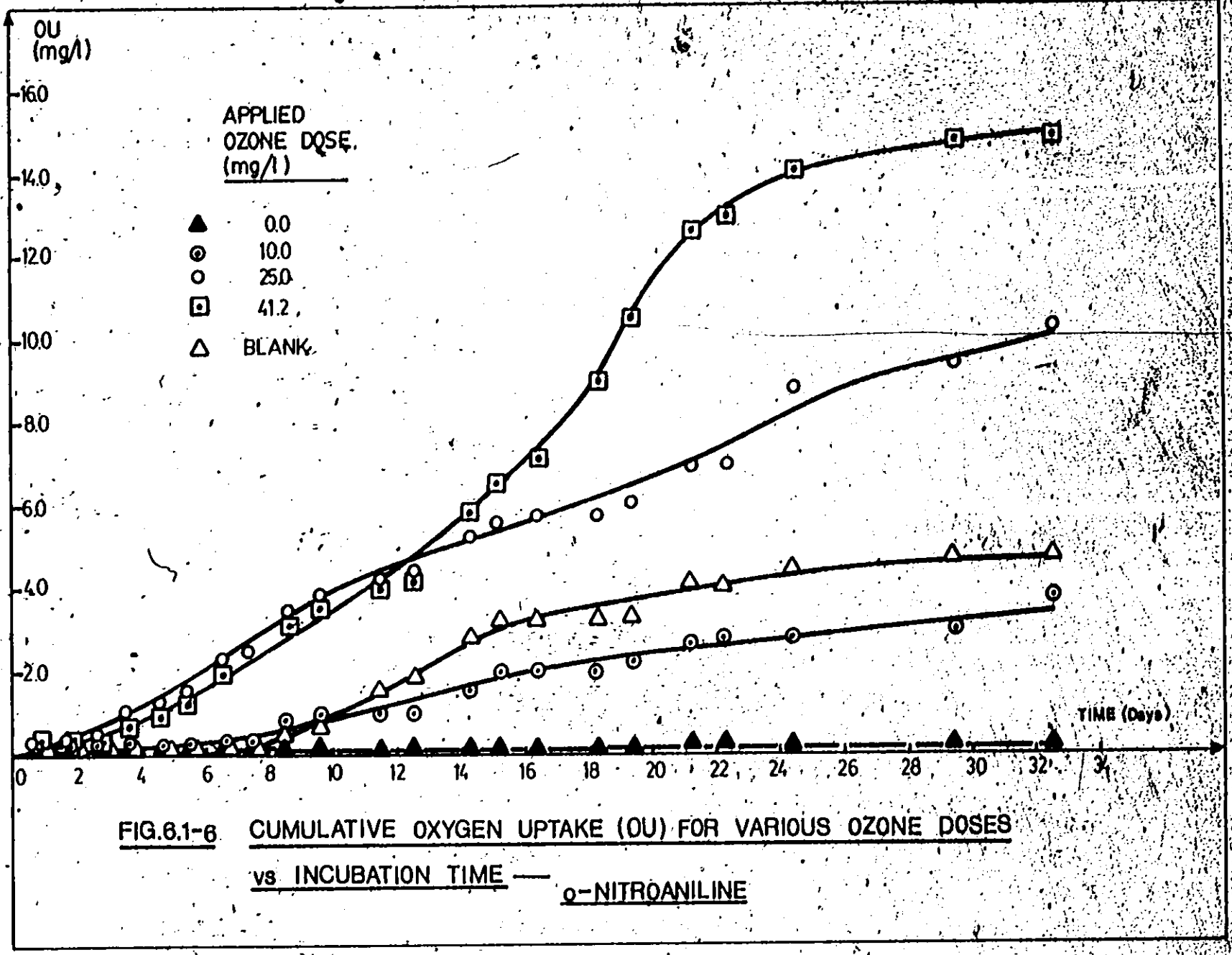
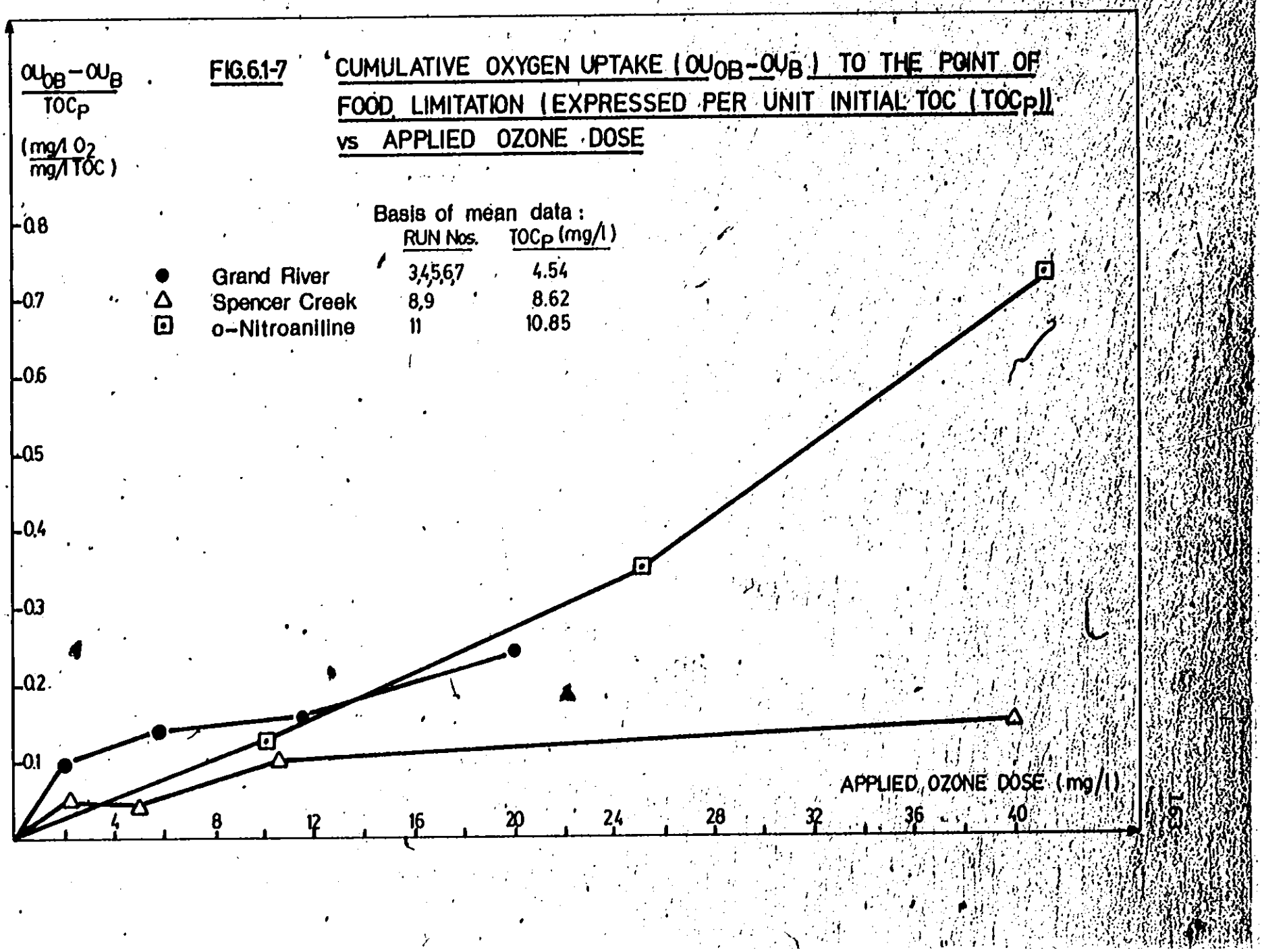


FIG.6.1-6 CUMULATIVE OXYGEN UPTAKE (OU) FOR VARIOUS OZONE DOSES vs INCUBATION TIME — o-NITROANILINE

FIG.6.1-7 CUMULATIVE OXYGEN UPTAKE ($OU_{OB}-OU_B$) TO THE POINT OF FOOD LIMITATION (EXPRESSED PER UNIT INITIAL TOC (TOC_P)) vs APPLIED OZONE DOSE



(iii) In general oxygen uptake increases with ozone level over the range of doses examined despite the reduced concentration of TOC after ozonation. Increased O_2 uptake is particularly evident in the case of ortho-nitroaniline (Run 11). No uptake was recorded for the unozonated sample, however nitrification in the blank resulted in significant oxygen uptake after 10 days incubation.

This trend is less evident for the Grand River and Spencer Creek runs. Although the mean data for Grand River water (runs 3-7), plotted in Figure 6.I-3, supports this claim the data in Appendix 6.1 shows considerable variation. While the highest oxygen uptake occurred after an ozone dose of 20 mg/ℓ (35 min. contact time) for all runs, inconsistences are apparent for the remaining ozone doses of 2, 6 and 12 mg/ℓ (corresponding to 3.5, 10, and 20 min. contact time respectively). Furthermore in runs 5 and 6 minimal oxygen uptake was observed for the two ozone doses applied. In all probability an optimum level of ozonation exists although ozone doses levels may not

have been sufficient to show this. In any event it may be concluded that the most effective use of ozone for these Grand River and Spencer Creek samples, in terms of oxygen uptake, is achieved at low ozone dose levels of approximately 2 mg/ℓ.

(iv) para-Nitroaniline (run 10, Fig. 6.1-5) was found to be biodegradable without ozonation. It is not clear why there is such an extended lag phase prior to rapid substrate removal as an acclimated seed was used. Carbon dioxide limitations, as discussed in the literature (Section 2.5.2) may be a possible explanation. For this run it is interesting to note that ozonation appears in fact to have inhibited biochemical activity as oxygen was not consumed after an ozone dose of 2 mg/ℓ. This effect may have resulted from the formation of toxic intermediate products.

(v) The oxygen uptake by ozonated o-nitroaniline samples greatly exceeded that of ozonated Spencer Creek samples for the same ozone dose even after linear corrections for differences in the untreated TOC are applied.

6.2 ORGANIC REMOVAL

6.2.1 TOC Reduction

Total Organic Carbon removal due to biodegradation ($\Delta TOC_{OB} = TOC_O - TOC_{OB}$) is shown in Figures 6.2-1, 6.2-2, and 6.2-3. Values have been corrected for biodegradation of the unozonated sample ($\Delta TOC_B = TOC_P - TOC_B$) and are expressed in terms of the initial unozonated sample TOC (TOC_P). The graphs are based on the data in Table A6.2 in Appendix 6 which has been compiled after correcting the Raw Data (Appendix 8.1) with the experiment blank ('TOC free' water).

Except for the already biodegradable p-nitroaniline TOC removal is improved by ozonation. Higher ozone doses result in greater, although progressively less effective, TOC reductions. For example the TOC reduction due to the biodegradation of o-nitroaniline after an ozone dose of 10 mg/ℓ was 18%, while 40 mg/ℓ ozone was required for 50% removal relative to the unozonated sample. The Grand River and Spencer Creek data again reflects the variability noted in Section 5. However it is noted that TOC removals are consistent with the oxygen uptake data. Improved TOC removal is matched by higher oxygen uptake (runs 4, 7, 8) and conversely low TOC removal by insignificant oxygen consumption (runs 5, 6). Greater TOC removal per unit initial TOC (TOC_P) occurs for Grand River

FIG.6.2-1 TOC REDUCTION BY BIODEGRADATION (ΔTOC_{OB}) CORRECTED FOR BIODEGRADATION OF THE UNOZONATED SAMPLE (ΔTOC_B) AND EXPRESSED AS A FRACTION OF THE INITIAL SAMPLE TOC (TOC_P) vs APPLIED OZONE DOSE — GRAND RIVER

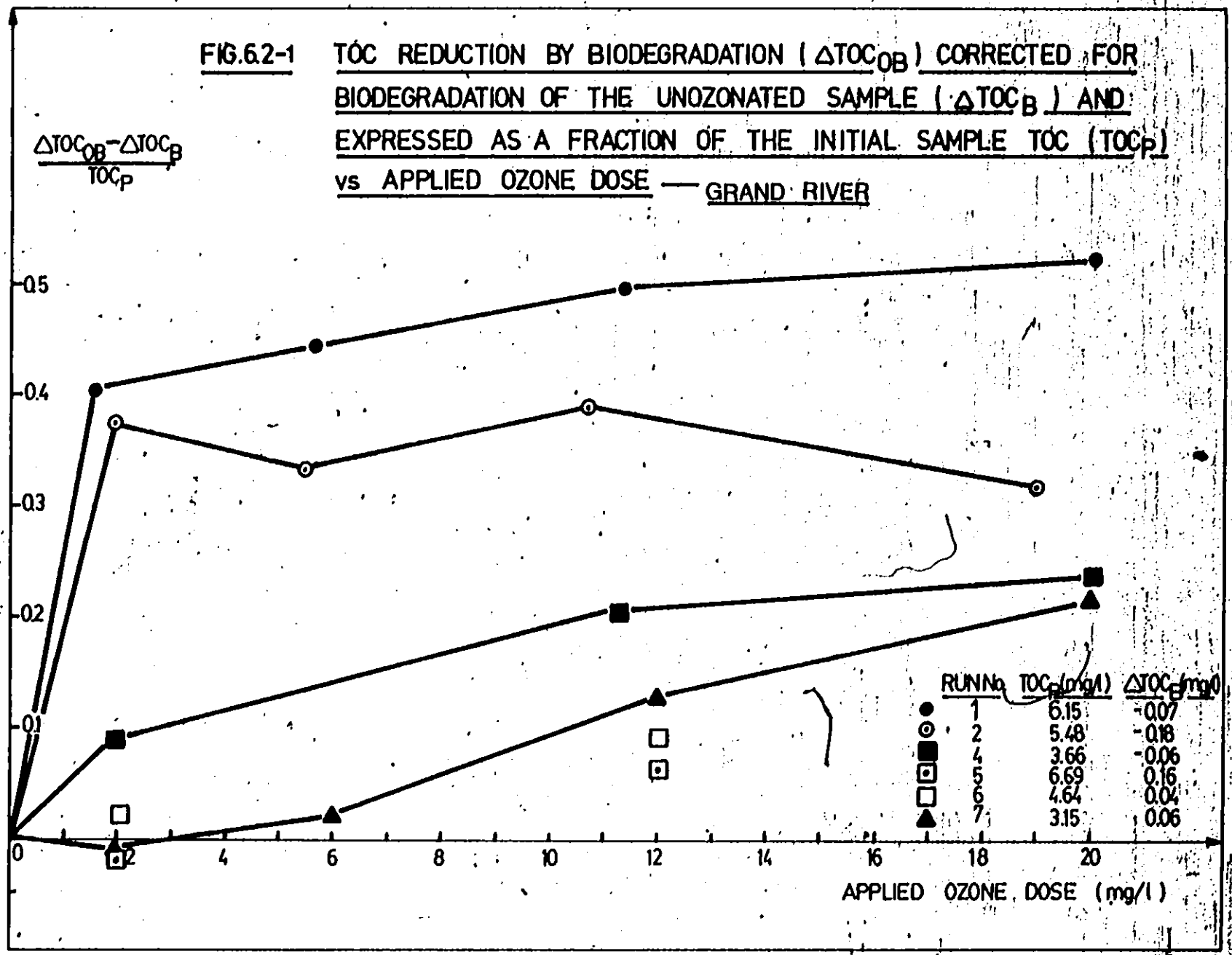


FIG.6.2-2 TOC REDUCTION BY BIODEGRADATION (ΔTOC_{OB}) CORRECTED FOR BIODEGRADATION OF THE UNOZONATED SAMPLE (ΔTOC_B) AND EXPRESSED AS A FRACTION OF THE INITIAL SAMPLE TOC (TOC_P) vs APPLIED OZONE DOSE — SPENCER CREEK

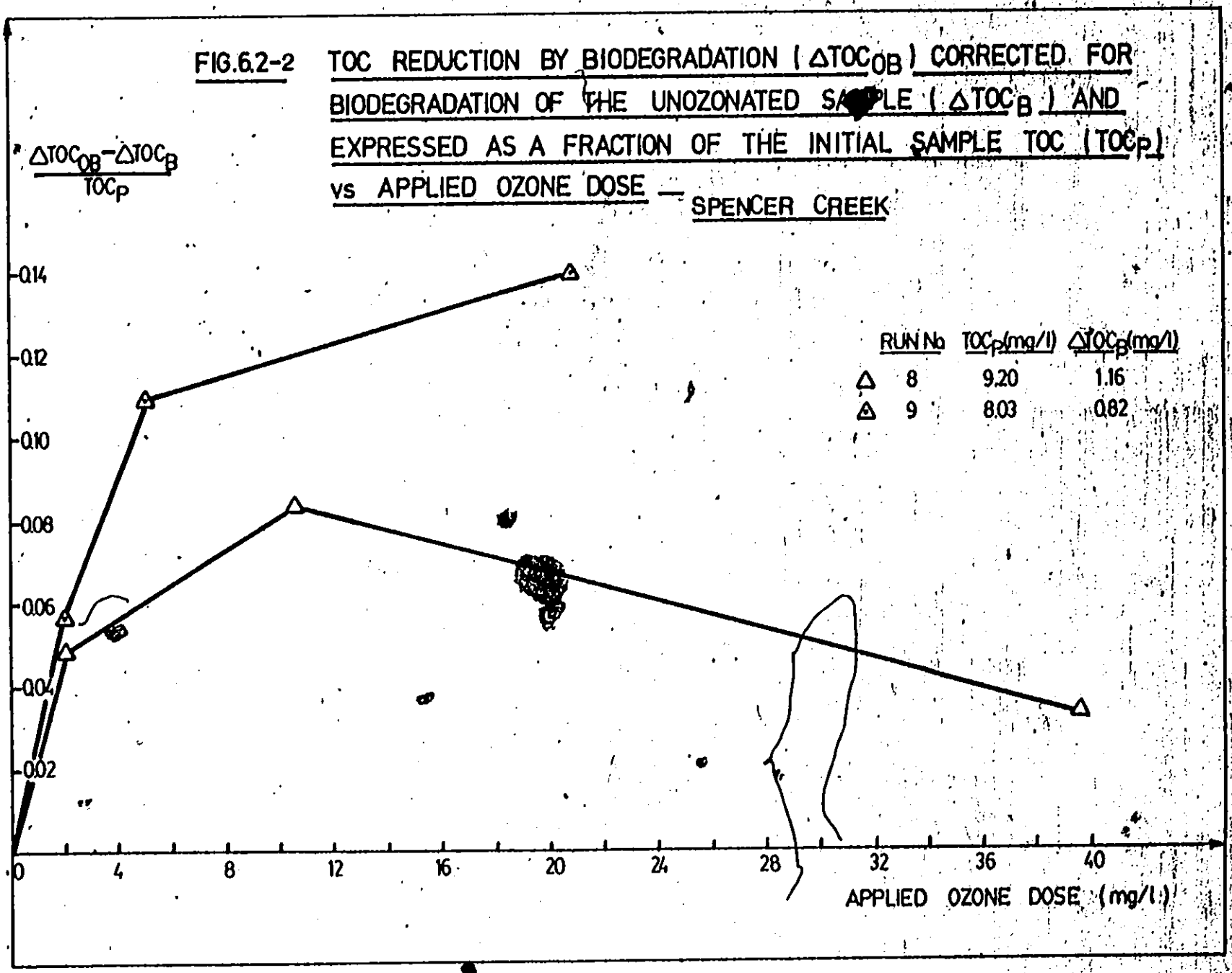
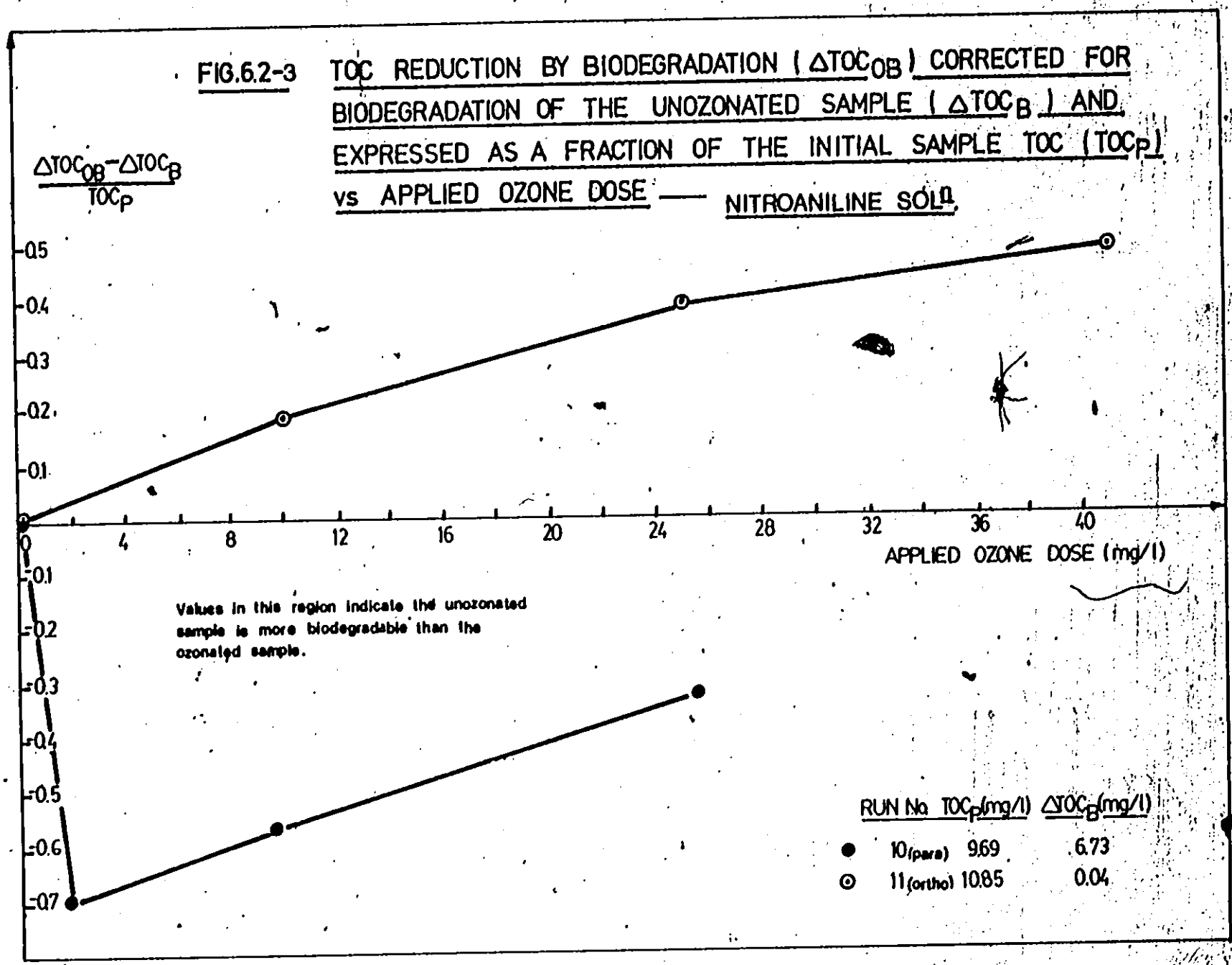


FIG.6.2-3 TOC REDUCTION BY BIODEGRADATION (ΔTOC_{OB}) CORRECTED FOR BIODEGRADATION OF THE UNOZONATED SAMPLE (ΔTOC_B) AND EXPRESSED AS A FRACTION OF THE INITIAL SAMPLE TOC (TOC_P) vs APPLIED OZONE DOSE —— NITROANILINE SOLⁿ.



samples than for those from Spencer Creek. It is likely that this effect is due to the presence of a wider variety of organic substances arising from man's influence on this water source. TOC removals due to the biodegradation of ozonated Grand River water are similar to those values reported in the literature for Rhine River water based on the improved performance of biologically enhanced granular activated carbon columns after ozonation. For example, at typical ozone doses of 2-5 mg/ℓ, Eberhardt et al. (1975) showed ozone improved the column TOC removal by 2 mg/ℓ compared with removals of 0.04-2.42 mg/ℓ for Grand River water in this study.

The results for p-nitroaniline (Fig. 6.2-3) indicate that all ozonated samples were less biodegradable than the raw. This may be attributed to the formation of inhibiting intermediates during ozonation.

6.2.2 UV Absorbance

In Figures 6.2-4 and 6.2-5 the UV absorbance after biodegradation (UV_{OB}) is shown as a fraction of the UV absorbance before biodegradation (UV_O). (Refer to Appendix 6, Table A6.2 for the data). Clearly there is little change in UV absorbance after biodegradation. Thus if UV absorbance can be considered a measure of the concentration of refractive substances in the untreated sample it

FIG.6.2-4 UV ABSORBANCE AFTER BIODEGRADATION (UV_{OB}) EXPRESSED AS A FRACTION OF THE ABSORBANCE BEFORE BIODEGRADATION (UV_O) vs APPLIED OZONE DOSE — GRAND RIVER

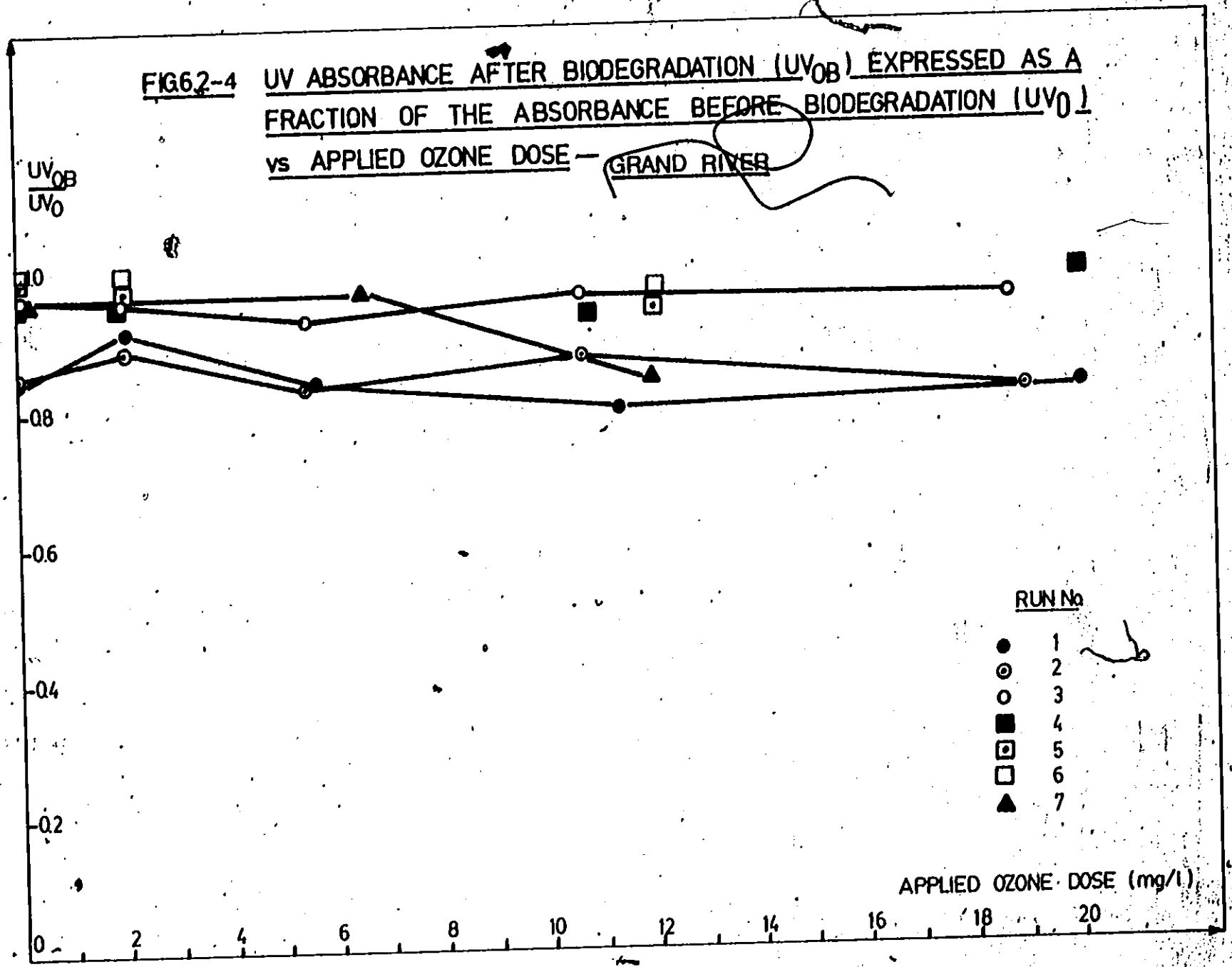
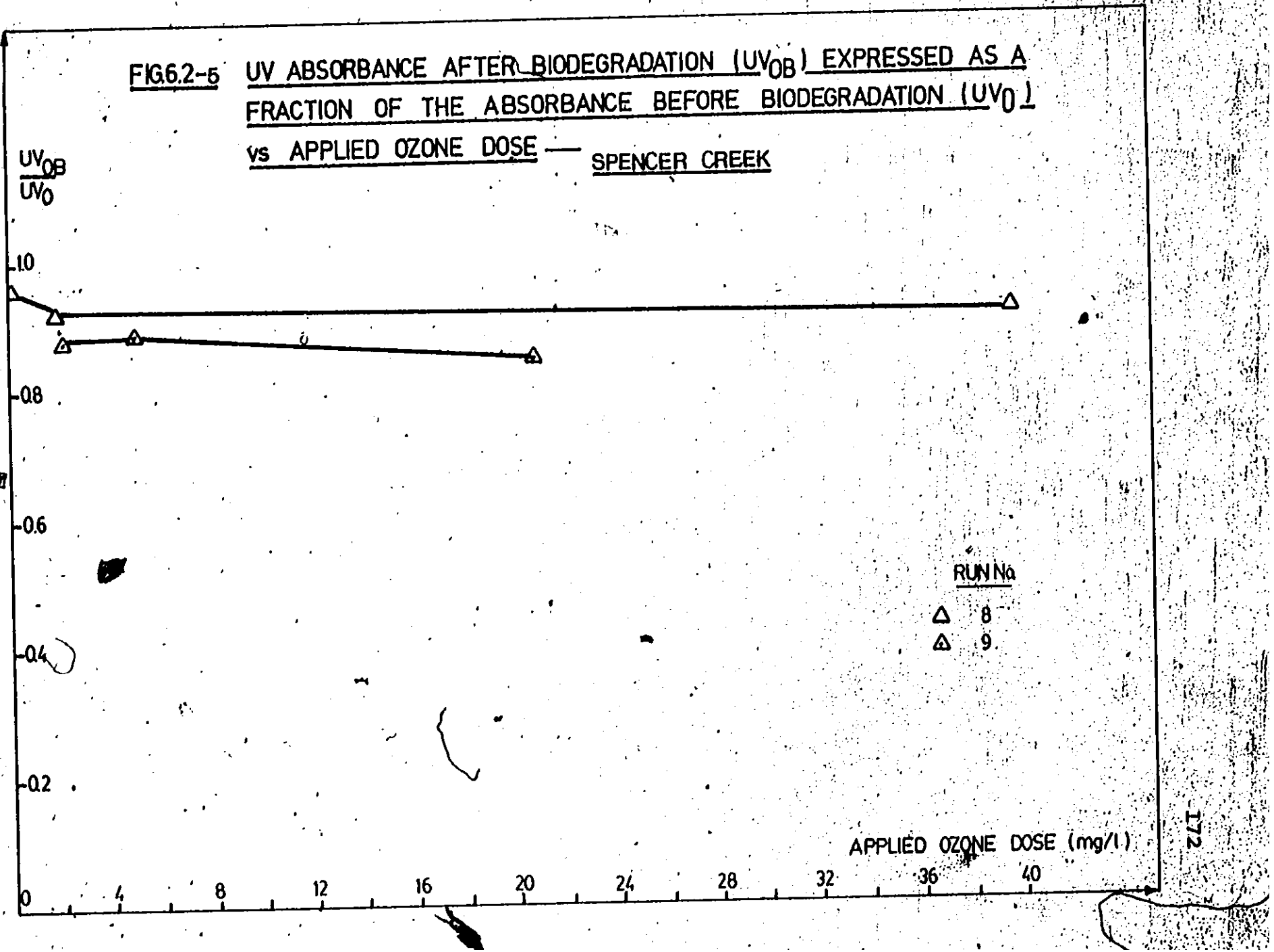


FIG.6.2-5 UV ABSORBANCE AFTER BIODEGRADATION (UV_{OB}) EXPRESSED AS A FRACTION OF THE ABSORBANCE BEFORE BIODEGRADATION (UV_O) vs APPLIED OZONE DOSE — SPENCER CREEK



may be assumed these compounds remained unaffected by incubation. As the UV absorbing organics remaining after ozonation represent, at least in part, the original sample no change in their concentration is expected during the biodegradation phase of the experiments. If this is the case then the TOC removal, and associated oxygen uptake, results from the biodegradation of those compounds formed by ozonation. The fact that biodegradation of the un-ozonated sample was minimal in most instances further supports this assertion.

6.3 NUTRIENT EFFECTS

The effect of nutrient addition was evaluated for Grand River water, run 4. Biodegradation studies were compared in duplicate for ozonated samples (20 min ozone contact) with and without nutrient addition. The results are shown in Table 6.3-1 based on the data in Table A8.1 and A8.2 of Appendix 8. No significant difference in TOC removal or oxygen uptake was observed for this run, thus suggesting the addition of nutrients may not be required. However nutrient addition was continued to ensure carbon was the limiting substrate.

TABLE 6.3-1

THE EFFECT OF NUTRIENT ADDITION FOR BIODEGRADABILITY EVALUATION (RUN 4)

Sample Description	Ozone Dose (mg/ℓ)	TOC_O[a] (mg/ℓ)	TOC_{OB}[b] (mg/ℓ)	UV_O 254nm 10cm	UV_{OB} 254nm 10cm	COD_O (mg/ℓ)	COD_{OB} (mg/ℓ)
Nutrients	11.2	2.90	2.25	0.406	0.408	6.9	5.0
No Nutrients	11.5	2.91	2.30	0.406	0.397	7.0	5.3

[a] Subscript '0' refers to the parameter value after ozonation.

[b] Subscript 'OB' refers to the parameter value after ozonation and biodegradation.

6.4 BIOCHEMICAL OXIDATION OF PARTIALLY OXIDIZED ORGANICS

In Section 5 the fraction, f, of partially oxidized organics was calculated for the ozonated samples (refer to Figures 5.4-4, 5.4-5, and 5.4-6). These values may now be compared with the extent of biodegradation assessed in terms of organic carbon removal (Figures 6.2-1, 6.2-2 and 6.2-3) and oxygen consumption. The mean oxygen uptake at the point of food limitation is shown in Fig. 6.4-1 as a function of f for each water source (the appro. data is shown in Table A6.3 of Appendix 6). There is good correlation between f and the subsequent biodegradation of ozonated nitroaniline samples. Both oxygen uptake and TOC removal consistently increase with higher values of f, which themselves correspond to higher ozone dose levels. This confirms the use of f as a means of postulating an improvement in sample biodegradability after ozonation. Data obtained for the Grand River and Spencer Creek samples does not clearly support this trend. Although the averaged data supports the trend an analysis of individual runs provides conflicting results which can only be explained in terms of experimental error and the variability of sample composition. While higher oxygen uptake is related to increased TOC removal there is little correlation of this with the f value for these runs. In summary, although the results with nitroaniline may justify the above approach, those obtained from the Grand River and Spencer Creek studies should be interpreted cautiously.

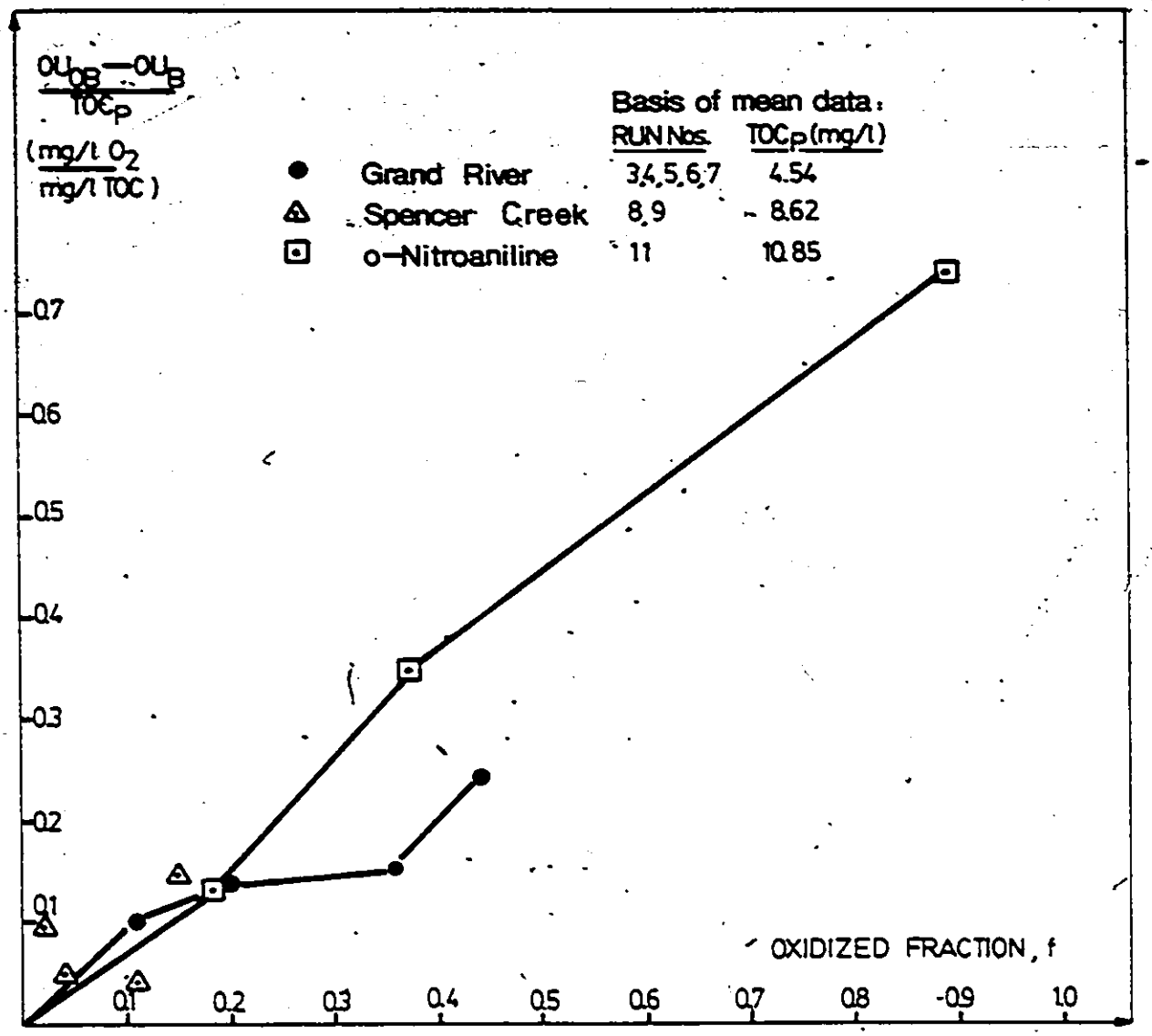


FIG.6.4-1 MEAN CUMULATIVE OXYGEN UPTAKE ($OU_{OB}-OU_B$) TO THE POINT OF FOOD LIMITATION (EXPRESSED PER UNIT OF INITIAL TOC (TOC_P)) vs THE PARTIALLY OXIDIZED FRACTION (f)

6.5 OVERALL TRENDS

6.5.1 Overall TOC Removal

In Figure 6.5-1 the combined TOC removal for ozonation and biodegradation is shown for each water source as a function of applied ozone dose. The TOC removal has been corrected for any biodegradation of the unozonated sample and expressed as a fraction of the initial TOC (TOC_p), based on the data in Appendix 7 (refer to Table A7.1).

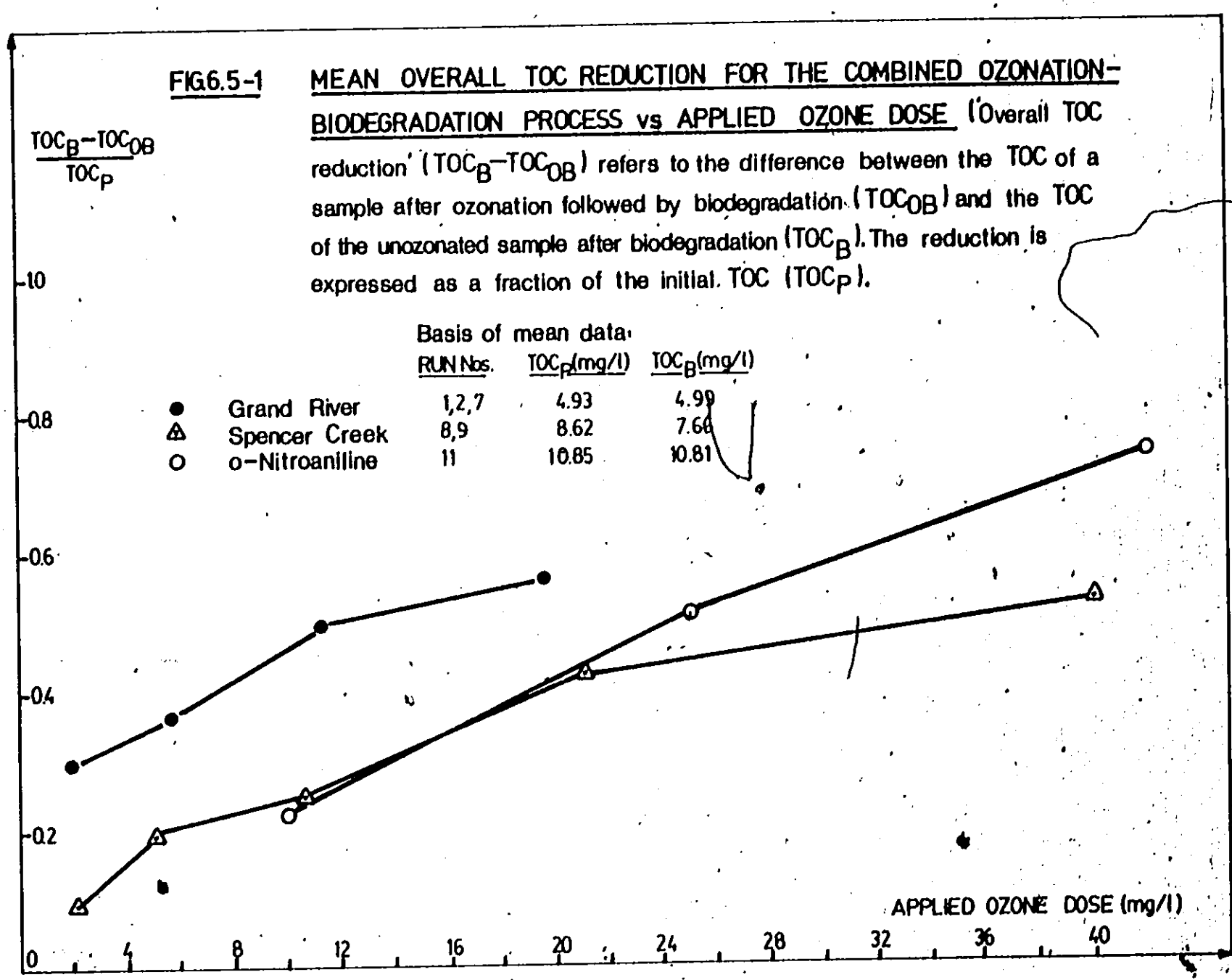
Increasing ozone dose results in increased TOC removal. For an ozone dose of 20 mg/ℓ the expected TOC removal for the combined ozonation-biodegradation process is in the range of 40-50% for each of the water sources. The range of TOC removals for the combined process are shown below in Table 6.5-1.

TABLE 6.5-1

OVERALL TOC REMOVAL FOR THE COMBINED OZONATION-BIODEGRADATION PROCESS

Water Source	Range of Applied Ozone Dose (mg/ℓ)	Range of TOC Removal (%)
Grand River	1.9 - 20.1	10 - 66
Spencer Creek	2.1 - 40.0	9 - 54
o-Nitroaniline	10.0 - 41.2	22 - 74

FIG.6.5-1 MEAN OVERALL TOC REDUCTION FOR THE COMBINED OZONATION-BIODEGRADATION PROCESS vs APPLIED OZONE DOSE ('Overall TOC reduction' ($TOC_B - TOC_{OB}$) refers to the difference between the TOC of a sample after ozonation followed by biodegradation (TOC_{OB}) and the TOC of the unozonated sample after biodegradation (TOC_B). The reduction is expressed as a fraction of the initial TOC (TOC_P).



6.5.2 Comparison of Ozonation and Biodegradation for TOC and COD Removal

The changes in COD and TOC due to ozonation and biodegradation may be compared so as to evaluate the relative significance of each process for TOC and COD removal respectively. In Appendix 7 the Figures A7.2-1, A7.2-2, and A7.2-3 show the change in COD after ozonation ($\Delta COD_O = COD_P - COD_O$) and after biodegradation ($\Delta COD_{OB} = COD_O - COD_{OB}$), expressed as a ratio ($\frac{\Delta COD_O}{\Delta COD_{OB} - \Delta COD_B}$). The biodegradation results have been corrected for changes in COD due to biodegradation of the unozonated sample ($\Delta COD_B = COD_P - COD_B$). The variation in TOC changes are similarly shown. Comparatively greater reductions in COD may be achieved by ozonation, and this effect is more pronounced at higher applied ozone doses. Conversely, except for the case of Spencer Creek, TOC changes for the biodegradation process are relatively more significant than for ozonation. This is based on the observation that $\frac{\Delta TOC_O}{\Delta TOC_{OB} - \Delta TOC_B}$ ratios are less than 1.0. The relative TOC removal, however, decreases as the applied ozone dose is increased. For the Spencer Creek samples TOC and COD removal was more significant for the ozonation process and this becomes more evident at higher ozone doses. A possible explanation may be the preferential oxidation of functional groups attached to the core of humic substances. The applied ozone doses have thus resulted in COD and TOC removal by ozonation but have not significantly improved the biodegradability of the core itself.

SECTION 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 CONCLUSIONS

The following conclusions can be drawn from this study:

1. A unique laboratory batch ozone contactor has been designed and built to successfully simulate typical ozonation practice in a full scale water treatment plant. In the normally applied ozone dose range of 2 to 10 mg/ℓ, greater than 90% ozone absorption is achieved for the ozonation of surface waters.
2. For the three water sources ozonated Total Organic Carbon (TOC) removal may be described by a first order process. Specific values of the first order reaction rate constant (k_{TOC}) were found to vary from 0.0041 min^{-1} for aqueous nitroaniline solutions to 0.023 min^{-1} for one Grand River water sample.
3. Ozonation resulted in more significant reductions in sample COD and UV absorbance relative to TOC removal, particularly for low applied ozone

doses. Increased oxidation of the original substrate is represented by a parameter f, describing the fraction of partially oxidized organics formed.

4. In addition to carbon oxidation, nitrogen containing substituent groups were oxidized to nitrate during the ozonation process.
5. Ozonation improved the biodegradability of dilute refractory organic substances in the water sources examined. This conclusion is based on the observed simultaneous removal of organic carbon and increase in oxygen uptake after ozonation.
6. For the ozone doses applied (0-40 mg/ℓ) higher ozone levels generally improved biodegradability. However the results show that ozone may be used most efficiently at low applied doses.
7. Higher values of the estimated fraction of partially oxidized organics, f, correlated well with improved biodegradability for the o-nitroaniline samples. TOC removal increased from 18 to 49% for values of f between 0.18 and 0.89. A similar analysis of the Grand River and Spencer Creek data, however, is inconclusive.

8. Despite significant TOC removal during biodegradation the concentration of UV absorbing substances remained approximately constant. The biodegradation of saturated or partially oxidized organics is therefore inferred.
9. p-Nitroaniline was shown to be biodegradable without ozonation. In fact biodegradation was inhibited by ozonation, especially at low ozone doses.
10. An important feature of the data is its variability. This is partly attributable to variations in sample composition and also experimental error associated with the dilute concentrations under consideration. For the ozonation of surface waters this variability underlines the necessity of multiple sample analysis over an extended period.
11. Substantial TOC removals were achieved by the combined ozonation-biodegradation process. While ozonation results in relatively greater changes in COD than TOC, the reverse is the case during biodegradation.

7.2 RECOMMENDATIONS

Based on the results of this study the following recommendations are proposed for future work:

1. Develop the ozone contactor model to describe the equipment performance when organic substances are present in the water. This would produce a more useful design for simulating full scale water treatment plant operation. A number of reaction rate constants are available in the literature for pure substrates and may be used for model verification.
2. The use of respirometers which are independent of atmospheric pressure should be evaluated for further biodegradability studies involving the measurement of low oxygen uptakes over an extended period. Modifications to the apparatus of Bridie (1969) may be suitable for a system with a controlled oxygen supply. With no atmospheric interference and minimal electrolyte evaporative loss it is anticipated this apparatus will provide more reproducible data. However consideration should be given to the possible formation of ozone, by electrolysis, if a copper sulphate solution is used as an electrolyte.

3. Examine the possible effect of carbon dioxide deficiency in respirometric biodegradability determinations. Organic removal may be compared for parallel biodegradation studies using respirometers and open vessels equipped with a glass filter cover to prevent atmospheric contamination. The effect of nutrient addition and the initial inoculum concentration on the rate of biodegradation should also be considered.
4. Compare the organic removal achieved using inoculated samples incubated in respirometers, with that obtained by filtration through an inert media, such as sand, on a continuous basis. Examine the effect of flow rate, residence time and bacterial seeding.

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APPENDIX I

MODEL FOR THE ABSORPTION OF OZONE INTO A GAS SPARGED BATCH REACTOR

A1.1 BULK LIQUID OZONE CONCENTRATION AS A FUNCTION OF TIME

The following derivation is based on the assumptions specified in Section 3.2. The contactor is thus shown schematically in Figure A1-1. A similar model is described by Shambaugh and Melnyk (1976).

Consider a mass balance over the reactor:

$$\begin{pmatrix}\text{Rate of ozone mass transfer}\\ \text{to the liquid}\end{pmatrix} = \begin{pmatrix}\text{rate of ozone}\\ \text{accumulation in}\\ \text{the bulk liquid}\end{pmatrix} + \begin{pmatrix}\text{rate of ozone}\\ \text{decomposition}\end{pmatrix} + \begin{pmatrix}\text{rate of ozone}\\ \text{chemical reaction}\end{pmatrix} \quad (1)$$

The total rate of ozone mass transfer to the liquid over the column height h is:

$$\frac{1}{h}\int_0^h k_L a(C^* - C)dx \quad (2)$$

The rate of ozone decomposition is: $k_d C^{3/2}$ (3)

The rate of ozone chemical reaction is: $k_r[S]\cdot C$ (4)

Then substituting (2), (3), and (4) in (1)

$$\frac{1}{h}\int_0^h k_L a(C^* - C)dx = \frac{dC}{dt} + k_d C^{3/2} + k_r[S]\cdot C \quad (5)$$

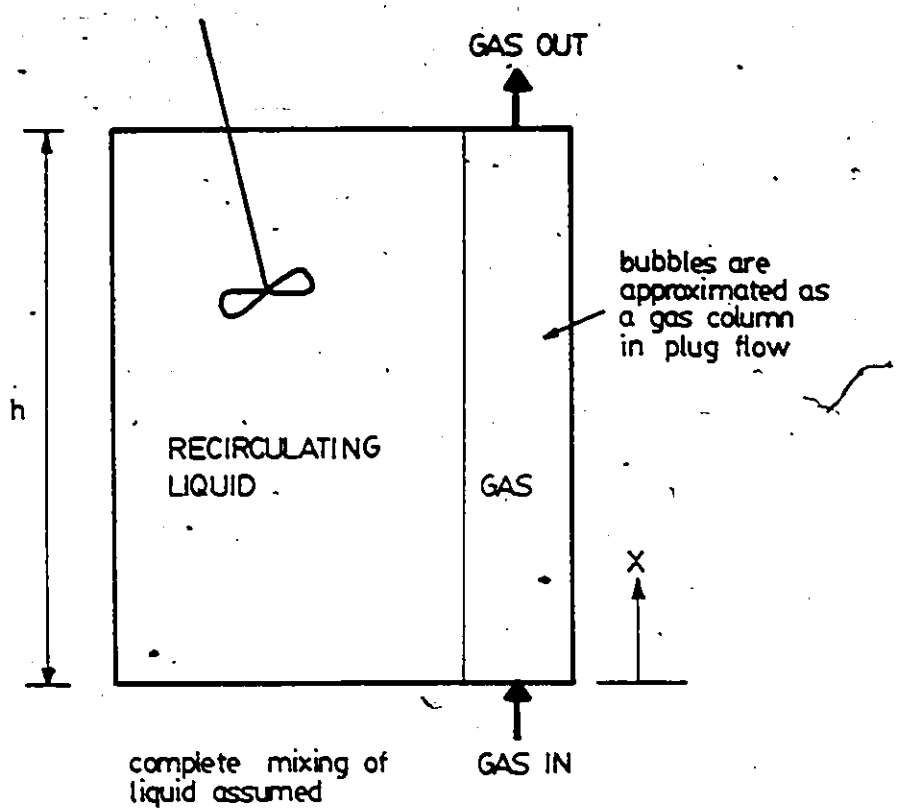


FIG.A1-1 SCHEMATIC OZONE CONTACTOR

The bulk liquid ozone concentration C, is independent of h, however the interfacial concentration C* is a function of column height. Assuming no accumulation in the interface the mass flux through the liquid phase equals the flux through the gas phase. Thus:

$$k_g P(y - y_i) = k_\ell (C^* - C) \qquad (6)$$

Applying Henry's law $y_i = \frac{K_H}{P} C^*$ and substituting in equation (6) and solving for C*:

$$C^* = \frac{\frac{k_g}{k_\ell} Py + C}{1 + \frac{k_g}{k_\ell} K_H} \qquad (7)$$

Substituting equation (7) into (5) and simplifying:

$$\frac{B}{h} \int_0^h (Py - K_H C)dx = \frac{dC}{dt} + k_d C^{3/2} + k_r[S] \cdot C \qquad (8)$$

where $B = \frac{k_\ell k_g a}{k_\ell + k_g K_H}$

y may be expressed as a function of C and x as follows: Consider a mass balance on ozone transferred across an elemental horizontal section of the column Δx,

mass in = mass out + mass transfered

$$G \frac{y}{1-y}\Big|_x = G \frac{y}{1-y}\Big|_{x + \Delta x} + \frac{\Delta x a V}{h} k_\ell (C^* - C) \qquad (9)$$

For small values of y (typical values do not exceed 0.03)

$\frac{y}{1-y} \approx y$. Substituting in equation (9), rearranging, dividing by Δx, and considering the limit as $\Delta x \to 0$:

$$G \frac{dy}{dx} = - \frac{aV}{h} k_\ell (C^* - C) \qquad (10)$$

Substituting equation (7) into (10) and rearranging gives:

$$\frac{dy}{dx} = -PDy + K_H DC \qquad (11)$$

where $D = \frac{BV}{Gh}$

Equation (11) is a linear differential equation. For the initial conditions $y = y_o$ at $x = 0$

$$y = \frac{K_H C}{P} + (y_o - \frac{K_H C}{P}) e^{-PDx} \qquad (12)$$

Then substituting for y in equation (5) and solving gives the desired equation describing the bulk liquid ozone concentration as a function of time:

$$- \frac{dC}{dt} = \frac{G}{V} (1 - e^{-PDh}) (y_o - \frac{K_H C}{P}) - k_d C^{3/2} - k_r [S] \cdot C \qquad (13)$$

A1.2 COMPUTER SOLUTION OF EQUATION (13)

The fourth order Runge-Kutta method may be used to solve equation (13) as shown in the programme below. Also calculated is the ozone concentration in the column exhaust gas based on equation (12). By way of example the appropriate input/output data is given for one of the conditions specified in Section 3.

Example: Model prediction of the ozone residual concentration for 'organic free' water as shown in Figure 3.3.2.

$G = 7.81 \times 10^{-4}$ moles $\cdot S^{-1}$

$V = 2.4 \times 10^{4}$ cm^3

$P = 1.25$ atm.

$h = 296$ cm

$y_o = 7.64 \times 10^{-3}$

$K_H = 67,680$ atm. cm^3. $mole^{-1}$ ...

International Critical Tables, 1928

$k_\ell a = 0.0029\ S^{-1}$...Experimental, refer Appendix 2

$k_d = 10.0\ (moles/cm^3)^{-\frac{1}{2}} \cdot S^{-1}$... Fitted parameter for tapwater

$k_r[S] = 0$ .... Solution free of organic substances.

Assuming liquid phase mass transfer is controlling and k_g is large:

$$D = \frac{V}{Gh} \cdot \frac{k_\ell a}{K_H}$$

The following relationships pertain to the programme listing:

$A = k_\ell a$

$A_1 = \frac{G}{V} \cdot y_o(1 - e^{-PDh})$

$A_2 = \frac{G}{V} \frac{K_H}{P}(1 - e^{-PDh})$

$A_3 = k_d$ CL = C H = 0.1

T = time (sec) XM = y

PROGRAMME LISTING AND PARTIAL OUTPUT

```
      PROGRAM TST (INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
      READ(5,1)A1,A2,A3,CL,H,A
    1 FORMAT(2F14.12,4F10.6)
      PRINT(6,51)A1,A2,A3
   51 FORMAT(2F15.12,F10.5)
      T=0.
      L=0
      PRINT(6,82)
      XM=0.
      CG=0.
      GO TO 22
   17 R1=CL*67680./1.25
      R2=(1.25*296.*24000.*A)/(0.000781*296.*67680.)
      XM=R1+(0.00764-R1)*EXP(-R2)
      CG=XM*48000./24.
   22 CLC=CL*.8000000.
      PRINT(6,81)T,CL,CLC,XM,CG
      L=L+1
      I=0
   18 CONTINUE
      F1=H*(A1-A2*CL-A3*CL**1.5)
      CL1=CL+0.5*F1
      F2=H*(A1-A2*CL1-A3*CL1**1.5)
      CL2=CL+0.5*F2
      F3=H*(A1-A2*CL2-A3*CL2**1.5)
      CL3=CL+F3
      F4=H*(A1-A2*CL3-A3*CL3**1.5)
      CL=CL+(F1+2.*F2+2.*F3+F4)/6.
      T=T+H
      I=I+1
      IF(I-300)16,17,17
   16 IF(L-20)18,40,40
   82 FORMAT(//,1X,"TIME(SECS)",3X,"CONC.(M/CM3)",5X,"CONC.(MG/L)",2X,"
     1GAS MOL FR.",2X,"GAS CONC.(MG/L)")
   81 FORMAT(2X,F10.1,3X,F13.10,4X,F10.2,2X,F10.5,6X,F10.2)
   40 STOP
      END
```

```
.000000000200   .001+16000000   10.00000
```

TIME(SECS)	CONC.(M/CM3)	CONC.(MG/L)	GAS MOL FR.	GAS CONC.(MG/L)
0.0	0.0000000000	0.00	0.00000	0.00
30.0	.0000000058	.28	.00173	3.40
60.0	.0000000112	.54	.00196	3.86
90.0	.0000000161	.78	.00218	4.29
120.0	.0000000206	.99	.00237	4.67
150.0	.0000000246	1.18	.00255	5.02
180.0	.0000000282	1.35	.00271	5.32
210.0	.0000000314	1.51	.00285	5.61
240.0	.0000000342	1.64	.00297	5.84
270.0	.0000000367	1.76	.00308	6.05
300.0	.0000000389	1.87	.00317	6.24
330.0	.0000000408	1.96	.00326	6.41
360.0	.0000000425	2.04	.00333	6.55
390.0	.0000000440	2.11	.00339	6.68
420.0	.0000000452	2.17	.00345	6.79
450.0	.0000000463	2.22	.00350	6.88
480.0	.0000000473	2.27	.00354	6.97
510.0	.0000000482	2.31	.00358	7.04
540.0	.0000000489	2.35	.00361	7.10
570.0	.0000000495	2.38	.00364	7.16

APPENDIX 2

ESTIMATION OF $k_\ell a$ FOR THE OZONE CONTACTOR

A2.1 THEORY

The $k_\ell a$ value for the ozone contactor is calculated assuming first order mass transfer of oxygen according to the film theory. Thus the gas transfer rate is proportional to the concentration gradient of the oxygen in solution expressed as:

$$\frac{dc}{dt} = k_\ell a(c_s - c) \qquad (1)$$

where, c = oxygen concentration at time, t (mg/ℓ)

c_s = saturation oxygen concentration (mg/ℓ)

k_ℓ = mass transfer coefficient (cm/sec)

a = interfacial area (cm^2/cm^3)

Integration of (1) for the initial condition $c = c_o$ at $t = 0$ gives:

$$\log_{10} \frac{(c_s - c)}{(c_s - c_o)} = - \frac{1}{2.303} k_\ell a, t \qquad (2)$$

Therefore the slope of the line obtained when $\log_{10} \frac{(c_s-c)}{(c_s-c_o)}$ is plotted as a function of t will be $- \frac{1}{2.303} k_\ell a$

A2.2 EXPERIMENTAL

A 24 ℓ sample of tap water (pH 8.3) was filtered through granular activated carbon to remove organic substances.

Sodium sulphite was added to deplete the dissolved oxygen concentration to zero. The sample was then pumped into the reactor and contacted with unozonated air at 1.05 ℓ/min. Sample reaeration was followed using a chart recorder and the output from a dissolved oxygen probe installed in the recirculation line.

A2.3 RESULTS

The results are recorded in Table A2.3-1 and plotted in Figure A2.3-1.

TABLE A2.3-1

DISSOLVED OXYGEN AS A FUNCTION OF TIME FOR THE AERATION OF TAPWATER

Time (mins)	Dissolved Oxygen Conc. (mg/ℓ)	$\frac{C_s - C^*}{C_s - C_o}$
0	0	1.0
2.4	2.5	0.71
4.8	4.3	0.51
7.2	5.8	0.33
9.6	6.9	0.21
12.0	7.5	0.14
14.4	7.9	0.09

* Initial dissolved oxygen conc. C_o = 0.0 mg/ℓ

Saturated dissolved oxygen conc. C_s = 8.7 mg/ℓ

Based on the slope of the line of best fit drawn in Figure A2.3.1

$$k_\ell a = \frac{2.303 \times 0.0748}{60} = 0.0029\ s^{-1}$$

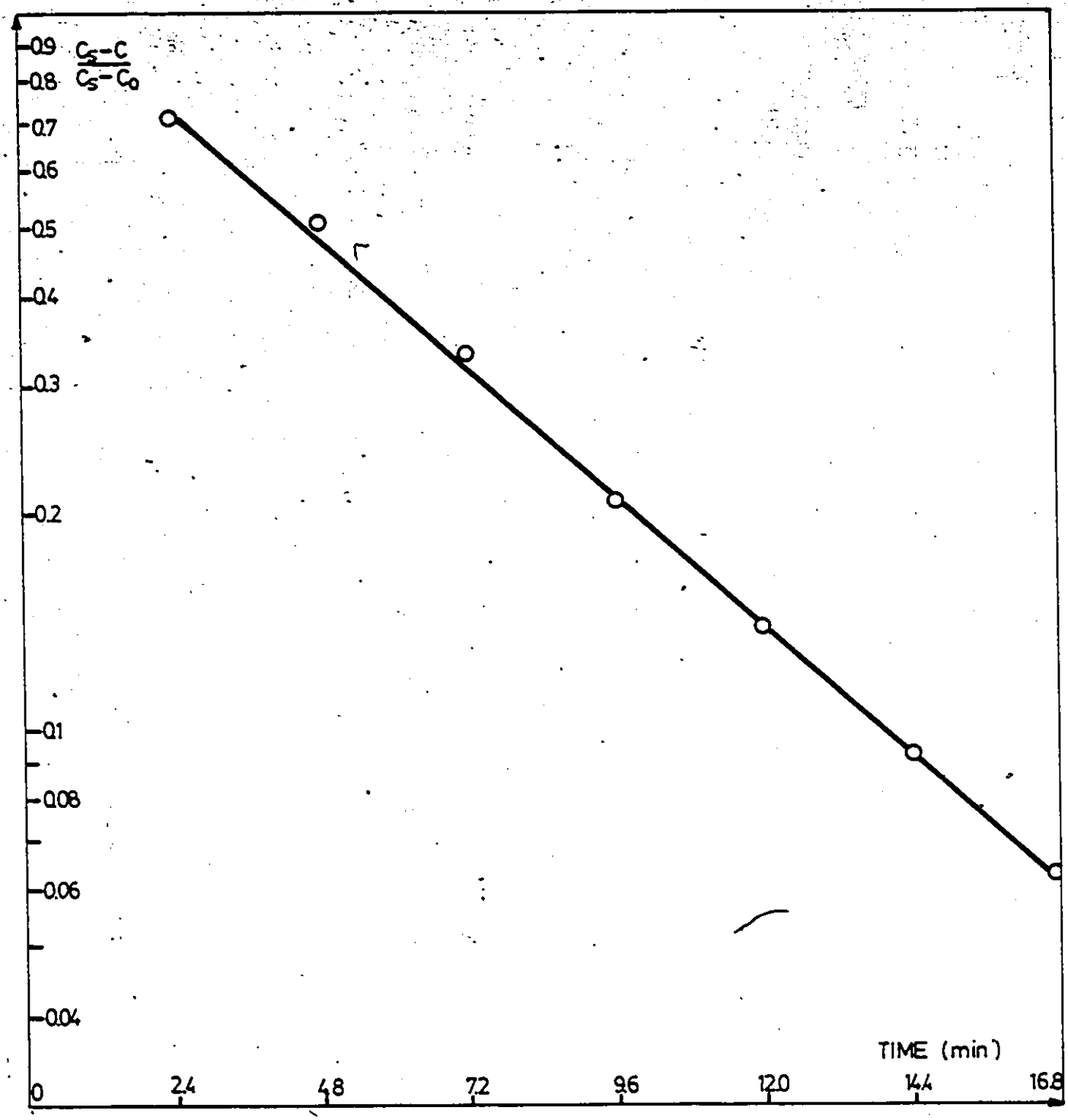


FIG.A2.3-1 PLOT OF $\frac{C_s-C}{C_s-C_o}$ AS A FUNCTION OF AERATION TIME

APPENDIX 3

GILMONT NO. 3 ROTAMETER CALIBRATION

A3.1 COLUMN OPERATION

The Gilmont No. 3 rotameter was fitted with a glass float. A P.S.I. Wet Test meter was installed after the two 500 mℓ scrubbers on the column exhaust gas line, and the rotameter calibrated under the following process conditions:

(i) Reaction column filled with 24.0 ℓ of water.

(ii) Each gas scrubber containing 500 mℓ of distilled water.

(iii) ~~Air~~ supply to the ozone generator at 0.7 bar.

In Table A3.1-1 the gas flowrate is tabulated for various rotameter settings, based on the time taken to collect a specified volume of gas.

A3.2 APPLIED GAS ANALYSIS

To determine the ozone concentration in the applied gas the contactor is bypassed, and the gas flow directed through two 500 mℓ gas scrubbers in series filled with a 2% potassium iodide solution. The pressure drop across this system is significantly different from normal contactor operation and therefore a separate calibration was required. The relevant data is presented in Table A3.2-1.

Calibration curves based on the information in Tables A3.1-1 and A3.2-1 are presented in Figure A3-1

TABLE A3.1-1

ROTAMETER CALIBRATION FOR TYPICAL COLUMN OPERATION

Rotameter Setting (%)	Pressure Drop (bar)	Gas Volume Collected (ℓ)	Collection Time (min:sec) Trial: 1	2	3	Gas Flow Rate (ℓ/min) 1	2	3	Mean Gas Flow (ℓ/min.)
	± 0.03	± 0.05	± 0:02			±0.02			
5	0.48	3.5	7:26	7:32		0.48	0.47		0.48
10	0.51	7.1	6:45	6:50	6:46[a]	1.05	1.04	1.05[a]	1.05
15	0.53	7.1	3:53	3:53		1.82	1.82		1.82
20	0.55	7.1	2:42	2.43		2.62	2.61		2.62
25	0.57	7.1	2:06			3.37			3.37

[a]Bypass in operation with gas flow rate to the ozone generator controlled at 3.20 ℓ/min.

TABLE A3.2-1

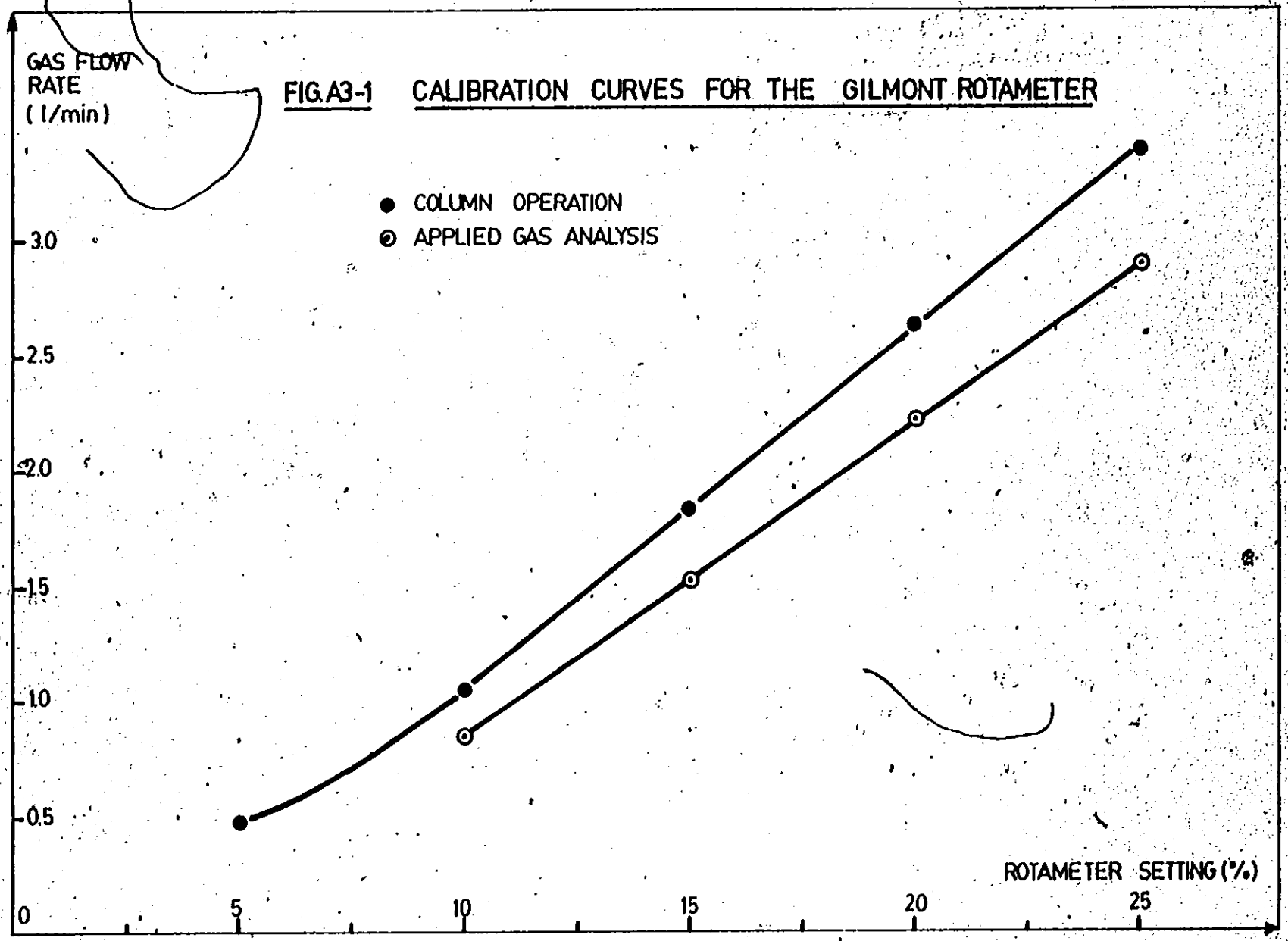
ROTAMETER CALIBRATION FOR APPLIED GAS ANALYSIS

Rotameter Setting (%)	Pressure Drop (bar)	Gas Volume Collected (ℓ)	Collection Time (min:sec) Trial:1	2	3	4	Gas Flow Rate (ℓ/min) 1	2	3	4	Mean Gas Flow (ℓ/min)
	±0.03	±0.05	±0:02				±0.02				
5[b]	-	-	-	-	-	-	-	-	-	-	-
10	0.12	7.1	8:32	8:28	8:28[a]	8:28[a]	0.83	0.84	0.84[a]	0.84[a]	0.84
15	0.16	7.1	4:41	4:38			1.51	1.53			1.52
20	0.17	7.1	3:12				2.21				2.21
25	0.19	7.1	2:27				2.89				2.89

[a]Bypass in operation with gas flow rate to the ozone generator controlled at 3.30 ℓ/min.

[b]Unstable flow control.

FIG.A3-1 CALIBRATION CURVES FOR THE GILMONT ROTAMETER



APPENDIX 4

OZONE CONTACTOR ABSORPTION PERFORMANCE

A4.1 Ozone Absorption as a Function of Applied Ozone Dose

A4.2 Sample Ozone Residual as a Function of Ozone Contact Time

A4.3 Mean Ozone Absorption as a Function of Applied Ozone Dose for Various Water Types

TABLE A4.1

OZONE ABSORPTION AS A FUNCTION OF APPLIED OZONE DOSE

Run No.	Ozone Contact Time (min)	Applied Gas $[O_3]$ (mg/ℓ)	Exhaust Gas $[O_3]$ (mg/ℓ)	Applied Ozone Dose (mg/ℓ)	Consumed Ozone Dose (mg/ℓ)	Utiliz.[n] (%)	Untreated Sample TOC_P (mg/ℓ)	Untreated Sample pH
Grand River Water								
0	3.5	14.23	0.43	2.18	2.11	97	5.48	8.3
	10.0	13.70	0.78	5.99	5.65	94	"	"
	20.0	13.55	1.77	11.86	10.31	87	"	"
	35.0	12.62	2.42	19.32	15.62	81	"	"
1	3.5	13.46	0.37	1.06	2.01	98	6.15	8.4
	10.0	12.97	0.54	5.67	5.45	96	"	"
	20.0	12.97	1.31	11.35	10.23	90	"	"
	35.0	13.11	2.93	20.06	15.59	78	"	"
2	3.5	12.61	0.29	1.93	1.89	98	5.48	8.3
	10.0	12.51	0.72	5.47	5.16	94	"	"
	20.0	12.22	1.48	10.69	9.40	88	"	"
	35.0	12.40	2.43	18.99	15.27	80	"	"
3	3.5	12.76	0.36	1.95	1.90	97	-	8.3
	10.0	12.46	0.92	5.45	5.05	93	-	"
	10.0[a]	12.83	3.42	5.61	4.12	73	-	"
	20.0	12.13	1.90	10.61	8.95	84	-	"
	35.0	12.23	3.28	18.73	13.70	73	-	"
4	3.5	12.61	0.28	1.93	1.89	98	3.65	8.4
	20.0	12.85	1.93	11.24	9.56	85	"	"
	20.0	13.08	2.01	11.45	9.69	85	"	"
	35.0	13.05	3.44	19.98	14.72	74	"	"
'TOC Free' Water								
A	10.0	12.73	4.89	5.57	3.43	62	0.41	6.5
B	10.0	13.96	3.85	5.93	4.30	73	0.62	6.5
C	10.0	18.10	3.03	7.69	6.40	83	-	6.8

[a] Sample pH adjusted to pH 3.0 with sulphuric acid prior to ozonation.

TABLE A4.1 (Cont'd)

Run No.	Ozone Contact (min)	Applied Gas $[O_3]$ (mg/ℓ)	Exhaust Gas $[O_3]$ (mg/ℓ)	Applied Ozone Dose (mg/ℓ)	Consumed Ozone Dose (mg/ℓ)	Utiliz.[n] (%)	Untreated Sample TOC_p (mg/ℓ)	Untreated Sample pH
Spencer Creek Water								
8	3.5	15.06	0.23	2.31	2.27	98	9.20	8.7
	20.0	12.14	0.39	10.62	10.28	97	"	"
	70.0	13.08	1.85	40.03	34.40	86	"	"
9	3.5	13.74	0.07	2.10	2.09	100	8.03	8.6
	8.5	13.60	0.39	5.06	4.91	97	"	"
	35.0	13.67	1.33	20.98	18.90	90	"	"
Aqueous p-Nitroaniline Solution								
10	3.5	12.61	0.00	1.93	1.93	100	9.69	8.1
	20.0	12.58	0.03	9.63	9.61	100	"	"
	45.0	12.98	0.09	25.55	25.38	99	"	"
Aqueous o-Nitroaniline Solution								
11	20.0	11.47	0.06	10.00	9.99	100	10.85	8.3
	45.0	12.70	0.14	25.00	24.72	99	"	"
	70.0	13.46	0.29	41.23	40.36	98	"	"

TABLE A4.2

SAMPLE OZONE RESIDUAL AS A FUNCTION OF OZONE CONTACT TIME

Sample Source	Ozone Contact Time (min)										
	1.0	3.0	3.5	4.0	7.5	8.0	10.0	11.0	12.5	13.5	15.0	30.0
'TOC Free' Water	0.14	1.43	-	-	-	2.15	-	2.58	-	-	2.36	2.66
Grand River	-	-	0.05	-	0.13	-	0.30	-	-	0.40	-	1.42
o-Nitroaniline (mg/ℓ)	-	-	0.00	-	-	0.00	-	-	0.00	-	-	0.00

TABLE A4.3

MEAN OZONE ABSORPTION AS A FUNCTION OF APPLIED OZONE DOSE FOR VARIOUS WATER TYPES

Sample Ozonated:	Distilled Water	Grand River Water				'Humic' Stream Water					Dilute Nitroaniline Soln			
pH	6.6	8.3	8.3	8.3	8.3	8.6	8.6	8.6	8.6	8.6	8.23	8.3	8.3	8.3
Total Organic Carbon (mg/ℓ)	0.60	5.27	5.27	5.27	5.27	8.62	8.03	9.20	8.03	9.20	9.69	10.27	10.27	10.85
Applied Ozone Dose (mg/ℓ)	6.4	2.0	5.7	11.2	19.4	2.2	5.1	10.6	21.0	40.0	1.9	9.8	25.3	41.2
Ozone Absorption (%)	72.3	97.5	94.4	86.5	77.1	98.9	97.1	96.7	90.1	85.9	100.0	99.9	99.1	97.9
Std. dev. (%)	10.6	0.5	1.4	2.2	3.6	0.8						0.1	0.3	
No. of runs	3	5	4	6	5	2	1	1	1	1	1	2	2	1

APPENDIX 5

CALCULATED DATA - OZONATION

A5.1 Soluble Organic Characteristics After Ozonation

A5.2 Total Organic Carbon Oxygen Demand Equivalent

A5.3 Ozonation Efficiency

TABLE A5.1

SOLUBLE ORGANIC CHARACTERISTICS AFTER OZONATION

Run No.	Applied Ozone Dose (mg/l)	TOC_P (mg/l)	TOC_O (mg/l)	ΔTOC_O (mg/l)	$\frac{TOC_O}{TOC_P}$	$\frac{\Delta TOC_O}{TOC_P}$	UV_P abs.	UV_O abs.	$\frac{UV_O}{UV_P}$	COD_P (mg/l)	COD_O (mg/l)	ΔCOD_O (mg/l)	$\frac{COD_O}{TOC_O}$	$\frac{O_3}{TOC_P}$	$f.COD_O$ (mg/l)	Oxidized fraction f	$\frac{O_3}{COD_P}$
Grand River Water																	
1	0.0	6.15	6.15	0.00	1.00	0.00	1.246	1.246	1.00	11.5	11.5	0.0	1.87	0.00	0.00	0.00	0.00
	2.1	"	6.05	0.10	0.98	0.02	"	0.824	0.66	"	11.2	0.3	1.85	0.34	0.01	0.00	0.18
	5.7	"	5.95	0.21	0.97	0.03	"	0.674	0.54	"	10.3	1.2	1.74	0.92	0.61	0.06	0.49
	11.4	"	5.62	0.53	0.91	0.09	"	0.526	0.42	"	9.9	1.6	1.75	1.85	0.23	0.02	0.99
	20.1	"	5.34	0.81	0.87	0.13	"	0.414	0.33	"	7.4	4.1	1.39	3.26	1.94	0.26	1.75
2	0.0	5.48	5.48	0.00	1.00	0.00	1.146	1.146	1.00	10.7	10.7	0.0	1.95	0.00	0.00	0.00	0.00
	1.9	"	5.36	0.12	0.98	0.02	"	0.807	0.70	"	10.5	0.2	1.96	0.35	0.00	0.00	0.18
	5.5	"	5.10	0.38	0.93	0.07	"	0.580	0.51	"	8.1	2.6	1.59	1.00	1.62	0.20	0.51
	10.7	"	4.64	0.84	0.85	0.15	"	0.441	0.39	"	7.0	3.8	1.50	1.95	1.55	0.22	1.00
	19.0	"	4.28	1.20	0.78	0.22	"	0.348	0.30	"	7.0	3.8	1.63	3.47	0.61	0.87	1.77
3	0.0	-	-	-	-	-	1.000	1.000	1.00	11.7	11.7	0.0	-	-	0.00	0.00	0.00
	2.0	-	-	-	-	-	"	0.663	0.66	"	9.8	1.9	-	-	-	-	-
	5.5	-	-	-	-	-	"	0.467	0.47	"	8.5	3.3	-	-	-	-	-
	10.6	-	-	-	-	-	"	0.356	0.36	"	8.3	3.5	-	-	-	-	-
	18.7	-	-	-	-	-	"	0.284	0.28	"	7.8	3.9	-	-	-	-	-
4	0.0	3.66	3.66	0.00	1.00	0.00	1.083	1.083	1.00	10.7	10.7	0.0	2.91	0.00	0.00	0.00	0.00
	1.9	"	3.53	0.13	0.96	0.04	"	0.772	0.71	"	8.8	1.9	2.49	0.53	1.51	0.17	0.18
	11.2	"	2.91	0.75	0.80	0.21	"	0.406	0.38	"	6.9	3.7	2.38	3.07	1.77	0.26	1.06
	20.0	"	2.52	1.14	0.69	0.31	"	0.310	0.29	"	6.4	4.3	2.53	5.46	1.30	0.20	1.88
5	0.0	6.69	6.69	0.00	1.00	0.00	1.860	1.860	1.00	12.7	12.7	0.0	1.90	0.00	0.00	0.00	0.00
	2.0	"	6.22	0.48	0.93	0.07	"	1.620	0.87	"	10.9	1.8	1.75	0.30	0.55	0.05	0.16
	12.0	"	4.87	1.82	0.73	0.27	"	0.922	0.50	"	5.8	6.9	1.19	1.79	2.13	0.37	0.95
6	0.0	4.64	4.64	0.0	1.00	0.00	1.224	1.224	1.00	10.2	10.2	0.0	2.20	0.00	0.00	0.00	0.00
	2.0	"	4.41	0.23	0.95	0.05	"	1.030	0.84	"	7.6	2.6	1.72	0.43	2.00	0.26	0.20
	12.0	"	3.01	1.63	0.65	0.35	"	0.460	0.38	"	4.0	6.2	1.33	2.59	1.93	0.48	1.18
7	0.0	3.15	3.15	0.00	1.00	0.00	0.894	0.894	1.00	7.3	7.3	0.0	2.32	0.00	0.00	0.00	0.00
	2.0	"	2.82	0.34	0.89	0.11	"	0.752	0.84	"	5.5	1.8	1.95	0.63	0.92	0.17	0.27
	6.0	"	2.48	0.67	0.79	0.21	"	0.443	0.50	"	4.1	3.2	1.65	1.90	1.45	0.35	0.82
	12.0	"	2.39	0.77	0.76	0.24	"	0.328	0.37	"	2.9	4.4	1.21	3.81	2.40	0.83	1.64
	20.0	"	2.21	0.95	0.70	0.30	"	0.217	0.24	"	2.2	5.1	1.00	6.34	2.61	1.19	2.74

TABLE A5.1 Cont'd

Run No.	Applied Ozone Dose (mg/ℓ)	TOC_P (mg/ℓ)	TOC_O (mg/ℓ)	ΔTOC_O (mg/ℓ)	$\frac{TOC_O}{TOC_P}$	$\frac{\Delta TOC_O}{TOC_P}$	UV_P[a] abs.	UV_O[a] abs.	$\frac{UV_O}{UV_P}$	COD_P (mg/ℓ)	COD_O (mg/ℓ)	ΔCOD_O (mg/ℓ)	$\frac{COD_O}{TOC_O}$	$\frac{O_3}{TOC_P}$	$f.COD_O$ (mg/ℓ)	Oxidized fraction f	$\frac{O_3}{COD_P}$
Spencer Creek Water																	
8	0.0	9.20	9.20	0.00	1.00	0.00	0.455	0.455	1.00	22.6	22.6	0.0	2.46	0.00	0.00	0.00	0.00
	2.3	"	8.88	0.32	0.97	0.04	"	0.392[b]	0.86	"	21.3	1.3	2.40	0.25	0.47	0.02	0.10
	10.6	"	7.55	1.65	0.82	0.18	"	0.100[b]	0.22	"	17.9	4.7	2.37	1.16	0.39	0.02	0.47
	40.0	"	4.57	4.63	0.50	0.50	"	0.100[b]	0.15	"	9.1	13.5	2.00	4.35	1.35	0.15	1.77
9	0.0	8.03	8.03	0.00	1.00	0.00	0.417	0.417	1.00	16.0	16.0	0.0	1.99	0.00	0.00	0.00	0.00
	2.1	"	7.67	0.36	0.96	0.04	"	0.365[b]	0.88	"	14.2	1.8	1.85	0.26	0.85	0.06	0.13
	5.1	"	7.37	0.66	0.92	0.08	"	0.195[b]	0.47	"	12.8	3.2	1.74	0.64	1.46	0.11	0.32
	21.0	"	5.60	2.43	0.70	0.30	"	0.113[b]	0.27	"	9.1	6.9	1.62	2.61	0.56	0.06	1.31
Aqueous p-Nitroaniline Solution																	
10	0.0	9.69	9.69	0.00	1.00	0.00	0.483	0.483	1.00	32.2	32.2	0.0	3.33	0.00	0.00	0.00	0.00
	1.9	"	9.63	0.06	0.99	0.01	"	0.499	1.03	"	30.4	1.8	3.15	0.20	1.64	0.05	0.06
	9.6	"	8.88	0.81	0.92	0.08	"	0.504	1.04	"	24.8	7.4	2.79	1.00	4.73	0.19	0.30
	25.6	"	7.88	1.82	0.81	0.19	"	0.365	0.76	"	20.0	12.2	2.54	2.64	6.18	0.31	0.79
Aqueous o-Nitroaniline Solution																	
11	0.0	10.85	10.85	0.00	1.00	0.00	0.738	0.738	1.00	30.6	30.6	0.0	2.82	0.00	0.00	0.00	0.00
	10.0	"	10.42	0.43	0.96	0.04	"	0.722	0.98	"	24.7	5.9	2.37	0.92	4.45	0.18	0.32
	25.0	"	9.58	1.27	0.88	0.12	"	0.535	0.73	"	19.2	11.4	2.01	2.31	7.15	0.37	0.82
	41.2	"	8.11	2.73	0.75	0.25	"	0.293	0.40	"	11.4	19.2	1.40	3.80	10.10	0.89	1.35

[a]Sample diluted 10:1 before analysis unless otherwise stated.

[b]Estimations based on the undiluted measurements tabulated in Appendix A8.1.

A5.2 TOTAL ORGANIC CARBON OXYGEN DEMAND EQUIVALENT

To calculate the fraction of partially oxidized organics after ozonation, as defined by Equation (5.4-1), the constant X, expressing TOC removal as an equivalent reduction in COD, must be known. The value of X is calculated below based on the following assumptions:

(i) The composition of organics in the Grand River and Spencer Creek samples is similar to that of Humic Substances.

(ii) The oxygen demand of Nitrogen is not recorded in the COD test.

(iii) The oxygen demand for the oxidation of sulphur is negligible.

(iv) Selective oxidation of specific functional groups is neglected.

(v) The oxygen in nitroaniline samples is not available for carbon oxidation.

(vi) TOC removal results from the oxidation of carbon to carbon dioxide.

Grand River and Spencer Creek Water

From the literature (Section 2.1.1) the mean composition of Humic Substances (HS) may be specified as:

Element	(%)	Moles/100 gms HS
C	50	4.17
O	42	2.63
H	5	5.00
N	2.5	0.18

Therefore the approximate molecular composition is:

$$C_{134}\ H_{161}\ O_{85}\ N_6\ S$$

The oxidation of this compound may then be written as:

$$131.5\ O_2 + C_{134}\ H_{161}\ O_{85}\ N_6 S \longrightarrow 134\ CO_2 + 80\ H_2O + \underset{\text{cmpds}}{N,S.}$$

∴ 131.5 moles of oxygen are required to oxidize 134 moles of C to carbon dioxide. Hence the TOC oxygen demand equivalent for the organics in these water sources is:

$$X = \frac{131.5 \times 32}{134 \times 12}$$

$$= 2.62\ \frac{\text{mg } O_2}{\text{mg TOC}}$$

Aqueous Nitroaniline Solution

It is assumed that the oxygen atoms in nitroaniline, being part of the $-NO_2$ group are not available for carbon

oxidation. Therefore the oxidation may be written as follows:

$$7.5\ O_2 + C_6\ H_6\ N_2\ O_2 \longrightarrow 6\ CO_2 + 3\ H_2O + N \text{ cmpds.}$$

∴ 7.5 moles of oxygen are required to oxidize 6 moles of C to carbon dioxide. Hence the TOC oxygen demand equivalent of nitroaniline in the COD test is:

$$X = \frac{7.5 \times 32}{6 \times 12}$$

$$= 3.33 \frac{\text{mg } O_2}{\text{mg TOC}}$$

TABLE A5.3 OZONATION EFFICIENCY

Run No.	Ozone Dose (mg/ℓ)	ΔCOD_O (mg/ℓ)	Eff. $\frac{\Delta COD_O}{O_3}$
Grand River Water			
1	2.1	0.3	0.14
	5.7	1.2	0.20
	11.4	1.6	0.14
	20.1	4.1	0.20
2	1.9	0.2	0.11
	5.5	2.6	0.48
	10.7	3.8	0.35
	19.0	3.8	0.20
3	2.0	1.9	0.98
	5.5	3.3	0.60
	10.6	3.5	0.33
	18.7	3.9	0.21
4	1.9	1.9	0.96
	11.2	3.7	0.33
	20.0	4.3	0.21
5	2.0	1.8	0.90
	12.0	6.9	0.58
6	2.0	2.6	1.30
	12.0	6.2	0.52
7	2.0	1.8	0.90
	6.0	3.2	0.53
	12.0	4.4	0.37
	20.0	5.1	0.26
Mean Data:			
	2.0		0.76
	5.7		0.45
	11.4		0.37
	19.6		0.22

TABLE A5.3 (Cont'd)

Run No.	Ozone Dose (mg/ℓ)	ΔCOD_O (mg/ℓ)	ΔNO_3-N_O (mg/ℓ)	ΔNO_2-N_O (mg/ℓ)	$\Delta COD_O + \Delta NOD_O$	Eff. $\frac{\Delta COD+\Delta NOD}{O_3}$
Spencer Creek Water						
8	2.3	1.3	0.12	0.00	1.85	0.80
9	2.1	1.8	0.05	0.00	2.01	0.96
Mean Data:						
	2.2					0.88
9	5.1	3.2	0.07	0.00	3.52	0.69
8	10.6	4.7	0.24	0.00	5.82	0.54
9	21.0	6.9	0.17	0.00	7.71	0.37
8	40.0	13.5	0.34	0.00	15.02	0.38
Aqueous Nitroaniline Solution						
10	1.9	1.9	0.05	0.07	2.03	1.05
	9.6	7.4	0.38	0.20	8.50	0.88
	25.6	12.2	1.17	0.12	15.03	0.59
11	10.0	5.9	0.40	0.13	6.93	0.70
	25.0	11.4	1.30	0.10	14.46	0.58
	41.2	19.2	1.99	0.04	23.78	0.58
Mean Data:						
	1.9					1.05
	9.8					0.79
	25.3					0.59
	41.2					0.58

APPENDIX 6

CALCULATED DATA - BIODEGRADATION

A6.1 Mean Oxygen Uptake

A6.2 Soluble Organic Removal Characteristics after Biodegradation

A6.3 Oxygen Uptake as a Function of the Partially Oxidized Organic Fraction

A6.1 OXYGEN UPTAKE

The oxygen uptake data in the following Tables are the mean values for duplicate runs and have been corrected for atmospheric pressure variation where this information is available.

TABLE A6.1-1 OXYGEN UPTAKE (mg/ℓ) FOR GRAND RIVER WATER - RUN 3

Ozone Contact (min)	Incubation Time (days)											
	0.9	2.0	3.1	3.9	5.0	5.9	7.1	7.9	9.1	10.0	10.9	11.9
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.07	0.07
3.5	0.08	0.08	0.13	0.32	0.32	0.47	0.49	0.57	0.83	0.83	0.95	0.95
10.0	0.06	0.06	0.14	0.31	0.32	0.55	0.75	0.82	1.12	1.12	1.28	1.31
10.0[a]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35.0	0.03	0.03	0.09	0.39	0.44	0.68	0.93	0.98	1.29	1.29	1.41	1.41
Blank	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.21	0.23	0.23	0.23

TABLE A6.1-2 OXYGEN UPTAKE (mg/ℓ) FOR GRAND RIVER WATER - RUN 4

Ozone Contact (min)	Incubation Time (days)							
	1.2	2.0	3.2	4.0	5.3	6.0	7.0	8.0
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3.5	0.00	0.00	0.24	0.46	0.75	0.89	1.01	1.01
20.0	0.07	0.07	0.34	0.52	0.76	0.91	1.03	1.03
35.0	0.00	0.00	0.01	0.33	0.72	1.08	1.20	1.38
Blank	0.00	0.00	0.00	0.00	0.00	0.33	0.51	0.51

[a]Sample ozonated at pH 3.0 and adjusted to pH 8.3 with sodium hydroxide prior to biodegradation.

TABLE A6.1-3

OXYGEN UPTAKE (mg/ℓ) FOR GRAND RIVER WATER - RUNS 5,6,7

Ozone Contact (min)	Incubation Time (days)									
	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0
Run 5[b]										
0.0	0.00	0.11	0.31	0.31	0.35	0.35	0.59	1.11	1.21	1.86
3.5	0.00	0.11	0.24	0.24	0.29	0.29	0.69	1.34	1.45	2.10
20.0	0.00	0.10	0.20	0.20	0.28	0.28	0.28	0.56	1.21	1.61
Run 6[b]										
0.0	0.00	0.13	0.20	0.20	0.25	0.25	0.34	0.71	0.71	0.85
3.5	0.00	0.23	0.32	0.32	0.42	0.42	0.65	1.04	1.04	1.18
20.0	0.00	0.10	0.19	0.19	0.20	0.20	0.68	1.27	1.30	1.52
Blank	0.00	0.19	0.62	0.90	1.21	1.36	1.83	2.38	2.38	2.62
Run 7										
0.0	0.00	0.03	0.03	0.03	0.03	0.03	0.41	0.78		
3.5	0.00	0.00	0.00	0.00	0.00	0.00	0.27	0.74		
10.0	0.00	0.10	0.10	0.10	0.10	0.10	0.70	1.12		
20.0	0.00	0.35	0.35	0.48	0.48	0.64	1.27	1.62		
35.0	0.00	0.28	0.28	0.42	0.42	0.77	1.32	1.62		
Blank	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.20		

[b] No parafilm enclosure on the respirometers and hence excessive electrolyte evaporative losses.

TABLE A6.1-4

MEAN OXYGEN UPTAKE (mg/ℓ) FOR GRAND RIVER WATER - RUNS 3,4,5,6,7

Ozone Contact (min)	Mean Incubation Time (days)									
	1.0	2.0	3.1	4.0	5.1	6.0	7.0	8.0	9.0	10.0
3.5	0.02	0.04	0.10	0.18	0.25	0.31	0.38	0.43	0.48	0.47
10.0	0.03	0.07	0.11	0.19	0.20	0.35	0.52	0.58	0.67	0.64
20.0	0.06	0.13	0.18	0.28	0.33	0.42	0.60	0.67	0.69	0.67
35.0	0.01	0.09	0.12	0.37	0.49	0.83	1.01	1.07	1.13	1.08

TABLE A6.1-5

OXYGEN UPTAKE (mg/ℓ) FOR SPENCER CREEK WATER - RUN 8

Ozone Contact (min)	Incubation Time (days)							
	0.5	2.4	3.4	5.5	7.4	8.4	9.4	12.4
0.0	0.01	1.34	1.34	1.49	1.49	1.49	1.49	1.49
3.5	0.01	1.45	1.51	1.89	2.00	2.00	2.00	2.00
17.5	0.04	1.32	1.38	1.78	2.18	2.40	2.44	2.62
70.0	0.03	1.33	1.48	2.01	2.52	2.74	2.78	2.93
Blank	0.00	0.98	0.98	0.98	0.98	0.98	0.98	1.31

TABLE A6.1-6

OXYGEN UPTAKE (mg/ℓ) FOR SPENCER CREEK WATER - RUN 9

Ozone Contact (min)	Incubation Time (days)							
	0.5	2.4	3.5	5.3	7.4	8.5	9.5	12.5
0.0	0.11	0.30	0.30	0.30	0.30	0.30	0.30	0.30
3.5	0.17	0.21	0.32	0.41	0.41	0.60	0.60	0.71
8.5	0.15	0.23	0.39	0.39	0.41	0.64	0.64	0.64
Blank	0.00	0.00	0.00	0.00	0.00	0.25	0.25	0.25

TABLE A6.1-7

OXYGEN UPTAKE (mg/ℓ) FOR p-NITROANILINE - RUN 10

Ozone Contact (min)	Incubation Time (days)												
	1.0	2.0	3.4	4.2	5.1	6.2	7.1	8.2	9.1	10.3	11.1	12.1	13.1
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.40	2.53	4.73	7.82
3.5	0.00	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
17.5	0.33	0.38	0.38	0.38	0.38	0.62	1.10	1.10	1.10	1.25	1.47	1.62	1.65
45.0	0.28	0.35	0.61	1.01	1.33	1.56	2.32	2.46	2.89	3.52	3.89	4.16	4.43
Blank	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.38	0.65	1.11	1.55	1.98

TABLE A6.1-8

OXYGEN UPTAKE (mg/ℓ) FOR o-NITROANILINE - RUN 11

Ozone Contact (min)	Incubation Time (days)																				
	0.5	1.6	2.4	3.5	4.5	5.3	6.5	7.4	8.5	9.5	11.3	12.5	14.2	15.2	16.3	18.2	19.3	21.2	22.2	24.3	29.4	32.5
0.0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.33	0.33	0.33	0.33	0.33
17.5	0.01	0.01	0.05	0.17	0.17	0.17	0.28	0.28	0.80	0.89	0.89	0.89	1.57	1.92	1.92	1.92	2.15	2.70	2.74	2.74	2.87	3.89
45.0	0.03	0.08	0.37	1.00	1.24	1.52	2.34	2.45	3.49	3.82	4.16	4.30	5.19	5.55	5.68	5.68	6.01	6.87	6.97	8.82	9.42	10.39
70.0	0.03	0.03	0.14	0.70	0.94	1.19	1.88	-	3.13	3.53	3.93	4.17	5.92	6.54	7.15	9.05	10.53	12.66	12.96	14.15	14.88	15.06
Blank	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.43	0.74	1.47	1.77	2.84	3.17	3.17	3.17	3.32	4.12	4.12	4.54	4.84	4.84

TABLE A6.2

SOLUBLE ORGANIC REMOVAL CHARACTERISTICS AFTER BIODEGRADATION

Run No.	Applied Ozone Dose (mg/ℓ)	TOC_P (mg/ℓ)	TOC_{OB} [a] (mg/ℓ)	ΔTOC_{OB} [b] (mg/ℓ)	$\frac{\Delta TOC_{OB} - \Delta TOC_B}{TOC_P}$	$\frac{UV_O}{UV_P}$	$\frac{UV_{OB}}{UV_O}$
Grand River Water							
1	0.0	6.15	6.22	-0.07	0.00	1.00	0.84
	2.1	"	3.63	2.42	0.41	0.66	0.91
	5.7	"	3.31	2.64	0.44	0.54	0.84
	11.4	"	2.64	2.99	0.50	0.42	0.79
	20.1	"	2.19	3.15	0.52	0.33	0.82
2	0.0	5.48	5.66	-0.18	0.00	1.00	0.85
	1.9	"	3.50	1.86	0.37	0.70	0.88
	5.5	"	3.47	1.64	0.33	0.51	0.82
	10.7	"	2.67	1.97	0.39	0.39	0.87
	19.0	"	2.72	1.56	0.32	0.30	0.81
3	0.0	-	-	-	-	1.00	0.97
	2.0	-	-	-	-	0.66	0.96
	5.5	-	-	-	-	0.47	0.93
	10.6	-	-	-	-	0.36	0.96
	18.7	-	-	-	-	0.28	0.95
4	0.0	3.66	3.72	-0.06	0.00	1.00	0.95
	1.9	"	3.27	0.26	0.09	0.71	0.95
	11.2	"	2.23	0.68	0.20	0.38	0.93
	20.0	"	1.71	0.81	0.24	0.29	0.99
5	0.0	6.69	6.53	0.16	0.00	1.00	0.99
	2.0	"	6.18	0.04	-0.02	0.87	0.97
	12.0	"	4.31	0.57	0.06	0.50	0.94
6	0.0	4.64	4.60	0.04	0.00	1.00	1.01
	2.0	"	4.28	0.13	0.02	0.84	1.00
	12.0	"	2.55	0.46	0.09	0.38	0.97
7	0.0	3.15	3.09	0.06	0.00	1.00	0.96
	2.0	"	2.78	0.04	-0.01	0.84	0.96
	6.0	"	2.36	0.12	0.02	0.50	0.97
	12.0	"	1.91	0.48	0.13	0.37	0.84
	20.0	"	1.45	0.75	0.22	0.24	1.24

TABLE A6.2 (Cont'd)

Run No.	Applied Ozone Dose (mg/ℓ)	TOC_P (mg/ℓ)	TOC_{OB} [a] (mg/ℓ)	ΔTOC_{OB} [b] (mg/ℓ)	$\frac{\Delta TOC_{OB} - \Delta TOC_B}{TOC_P}$	$\frac{UV_O}{UV_P}$	$\frac{UV_{OB}}{UV_O}$
Spencer Creek Water							
8	0.0	9.20	8.10	1.10	0.00	1.00	0.96
	2.3	"	7.34	1.54	0.05	0.86	0.92
	10.6	"	5.68	1.87	0.08	0.22	-
	40.0	"	3.17	1.40	0.03	0.15	0.92
9	0.0	8.03	7.21	0.82	0.00	1.00	0.96
	2.1	"	6.40	1.27	0.06	0.88	0.89
	5.1	"	5.66	1.71	0.11	0.47	0.88
	21.0	"	3.65	1.94	0.14	0.27	0.85
Aqueous p-Nitroaniline Solution							
10	0.0	9.69	2.96	6.73	0.00	1.00	0.62
	1.9	"	9.64	-0.01	-0.67	1.03	0.96
	9.6	"	7.66	1.23	-0.60	1.04	0.87
	25.6	"	4.29	3.58	-0.43	0.76	0.81
Aqueous o-Nitroaniline Solution							
11	0.0	10.85	10.81	0.04	0.00	1.00	-
	10.0	"	8.39	2.03	0.18	0.98	-
	25.0	"	5.35	4.22	0.39	0.73	-
	41.2	"	2.82	5.29	0.49	0.40	-

[a,b] Terminology for the unozonated sample i.e. ozone dose of 0.0, is TOC_B, ΔTOC_B resp.

TABLE A6.3

OXYGEN UPTAKE AS A FUNCTION OF THE PARTIALLY OXIDIZED ORGANIC FRACTION

Run No.	Applied Ozone Dose (mg/ℓ)	TOC_P (mg/ℓ)	Ozone Oxidized Fraction f	Oxygen[a] Uptake to Food limit[n] $OU_{OB}-OU_B$ (mg/ℓ)	Nitrogenous[c] Oxygen Uptake NOU (mg/ℓ)	Carbonaceous $OU_{OB}-OU_B-NOU$ (mg/ℓ)	$\frac{OU_{OB}-OU_B-NOU}{TOC_P}$
Aqueous o-Nitroaniline Solution							
11	10.0	10.85	0.18	4.7	3.3[c]	1.4	0.13
	25.0	"	0.37	10.3	6.5	3.8	0.35
	41.2	"	0.89	15.0	7.1	7.9	0.74
Spencer Creek Water							
8,9	2.2	8.62	0.04	0.39	0.0	0.39	0.05
9	5.1	8.03	0.11	0.35	0.0	0.35	0.04
8	10.6	9.20	0.02	0.90	0.0	0.90	0.10
8	40.0	9.20	0.15	1.25	0.0	1.25	0.15
Grand River Water							
Mean of Runs 3-7	2.0	4.54	0.11[b]	0.46	0.0	0.46	0.10
	5.8	"	0.20	0.63	0.0	0.63	0.14
	11.6	"	0.36	0.68	0.0	0.68	0.15
	19.6	"	0.44	1.10	0.0	1.10	0.24

[a]For o-Nitroaniline this is taken as the Total Oxygen Uptake and includes nitrification. Spencer Creek and Grand River water to reach plateau prior to onset of nitrification.

[b]Oxidized fractions for Grand River water calculated as the mean of runs 1-7.

[c]Nitrogenous Oxygen Uptake is based on the change in Nitrite and Nitrate concentrations due to biodegradation. These changes are recorded in Appendix A8.1.

APPENDIX 7

CALCULATED DATA - OVERALL OZONATION/ BIODEGRADATION TREATMENT

A7.1 Combined Ozonation/Biodegradation Total Organic Carbon Removal

A7.2 TOC and COD Characteristics for the Ozonation and Biodegradation processes

TABLE A7.1

COMBINED OZONATION/BIODEGRADATION

TOTAL ORGANIC CARBON REMOVAL

Run No.	Applied Ozone Dose (mg/ℓ)	TOC_P (mg/ℓ)	TOC_B (mg/ℓ)	TOC_{OB} (mg/ℓ)	$\frac{TOC_B - TOC_{OB}}{TOC_P}$
Grand River Water					
1	2.1	6.15	6.22	3.63	0.42
	5.7	"	"	3.31	0.47
	11.4	"	"	2.64	0.58
	20.1	"	"	2.19	0.66
2	1.9	5.48	5.66	3.50	0.39
	5.5	"	"	3.47	0.40
	10.7	"	"	2.67	0.55
	19.0	"	"	2.72	0.54
7	2.0	3.15	3.09	2.78	0.10
	6.0	"	"	2.36	0.23
	12.0	"	"	1.91	0.37
	20.0	"	"	1.45	0.52
Mean Data:					
	2.0				0.30
	5.7				0.37
	11.4				0.50
	19.7				0.57

TABLE A7.1 (Cont'd)

Run No.	Applied Ozone Dose (mg/ℓ)	TOC_P (mg/ℓ)	TOC_B (mg/ℓ)	TOC_{OB} (mg/ℓ)	$\frac{TOC_B - TOC_{OB}}{TOC_P}$
Spencer Creek Water					
8	2.3	9.20	8.10	7.34	
9	2.1	8.03	7.21	6.40	
Mean	2.2	8.62	7.66	6.87	0.09
9	5.1	8.03	7.21	5.66	0.19
8	10.6	9.20	8.10	5.68	0.26
9	21.0	8.03	7.21	3.65	0.44
8	40.0	9.20	8.10	3.17	0.54
Aqueous o-Nitroaniline Solution					
11	10.0	10.85	10.81	8.39	0.22
	25.0	"	"	5.35	0.50
	41.2	"	"	2.82	0.74

TABLE A7.2

TOC AND COD CHARACTERISTICS FOR THE OZONATION AND BIODEGRADATION PROCESSES

Run No.	Applied Ozone Dose (mg/ℓ)	ΔTOC_O (mg/ℓ)	ΔCOD_O (mg/ℓ)	ΔTOC_{OB} (mg/ℓ)	ΔCOD_{OB} (mg/ℓ)	$\frac{\Delta COD_O}{\Delta TOC_O}$	$\frac{\Delta COD_{OB}-\Delta COD_B}{\Delta TOC_{OB}-\Delta TOC_B}$	$\frac{\Delta COD_O}{\Delta COD_{OB}-\Delta COD_B}$	$\frac{\Delta TOC_O}{\Delta TOC_{OB}-\Delta TOC_B}$
Grand River Water									
1	0.0	0.00	0.0	-0.07	-0.3				
2	0.0	0.00	0.0	-0.18	2.3				
7	0.0	0.00	0.0	0.07	0.0				
Mean	0.0	0.00	0.0	-0.11	0.7				
1	2.1	0.10	0.3	2.42	4.6				
2	1.9	0.12	0.2	1.86	4.0				
7	2.0	0.34	1.8	0.04	0.3				
Mean	2.0	0.19	0.8	1.44	2.9	4.1	1.5	0.34	0.12
1	5.7	0.21	1.2	2.64	4.9				
2	5.5	0.38	2.6	1.64	2.3				
7	6.0	0.67	3.2	0.12	0.7				
Mean	5.7	0.42	2.3	1.47	2.6	5.6	1.2	1.19	0.27
1	11.4	0.53	1.6	2.99	5.5				
2	10.7	0.85	3.8	1.97	2.0				
7	12.0	0.77	4.4	0.48	0.6				
Mean	11.4	0.71	3.3	1.81	2.7	4.6	1.1	1.60	0.37
1	20.1	0.81	4.1	3.15	4.0				
2	19.0	1.20	3.8	1.56	3.0				
7	20.0	0.95	5.1	0.75	0.2				
Mean	19.7	0.99	4.3	1.82	2.4	4.4	0.9	2.48	0.51

TABLE A7.2 (Cont'd)

Run No.	Applied Ozone Dose (mg/ℓ)	ΔTOC_O (mg/ℓ)	ΔCOD_O (mg/ℓ)	ΔTOC_{OB} (mg/ℓ)	ΔCOD_{OB} (mg/ℓ)	$\frac{\Delta COD_O}{\Delta TOC_O}$	$\frac{\Delta COD_{OB}-\Delta COD_B}{\Delta TOC_{OB}-\Delta TOC_B}$	$\frac{\Delta COD_O}{\Delta COD_{OB}-\Delta COD_B}$	$\frac{\Delta TOC_O}{\Delta TOC_{OB}-\Delta TOC_B}$
Spencer Creek Water									
8	0.0	0.00	0.0	1.10	3.7				
9	0.0	0.00	0.0	0.82	0.8				
Mean	0.0			0.96	2.2				
8	2.3	0.32	1.3	1.54	6.6				
9	2.1	0.36	1.8	1.27	1.5				
Mean	2.2	0.34	1.5	1.41	4.0	4.6	3.9	0.87	0.75
9	5.1	0.66	3.2	1.71	2.2	4.8	2.0	-	0.89
8	10.6	1.65	4.7	1.87	6.0	2.9	4.1	1.26	1.80
9	21.0	2.43	6.9	1.94	3.7	2.9	1.4	4.9	2.47
8	40.0	4.63	13.5	1.40	2.5	2.9	0.7	45.7	10.49
Aqueous o-Nitroaniline Solution									
11	0.0	0.00	0.0	0.04	-1.6				
	10.0	0.43	5.9	2.03	3.3	13.7	2.5	1.20	0.22
	25.0	1.27	11.4	4.22	4.3	9.0	1.4	1.93	0.30
	41.2	2.73	19.2	5.29	5.0	7.0	1.2	2.93	0.52

FIG. A7.2-1 RELATIVE REMOVAL OF COD AND TOC BY OZONATION ($\frac{\Delta COD_O}{\Delta COD_{OB} - \Delta COD_B}$, $\frac{\Delta TOC_O}{\Delta TOC_{OB} - \Delta TOC_B}$) AND BIODEGRADATION ($\frac{\Delta COD_{OB} - \Delta COD_B}{\Delta COD_{OB}}$, $\frac{\Delta TOC_{OB} - \Delta TOC_B}{\Delta TOC_{OB}}$) vs APPLIED OZONE DOSE

GRAND RIVER (Mean of runs 1, 2, 7)

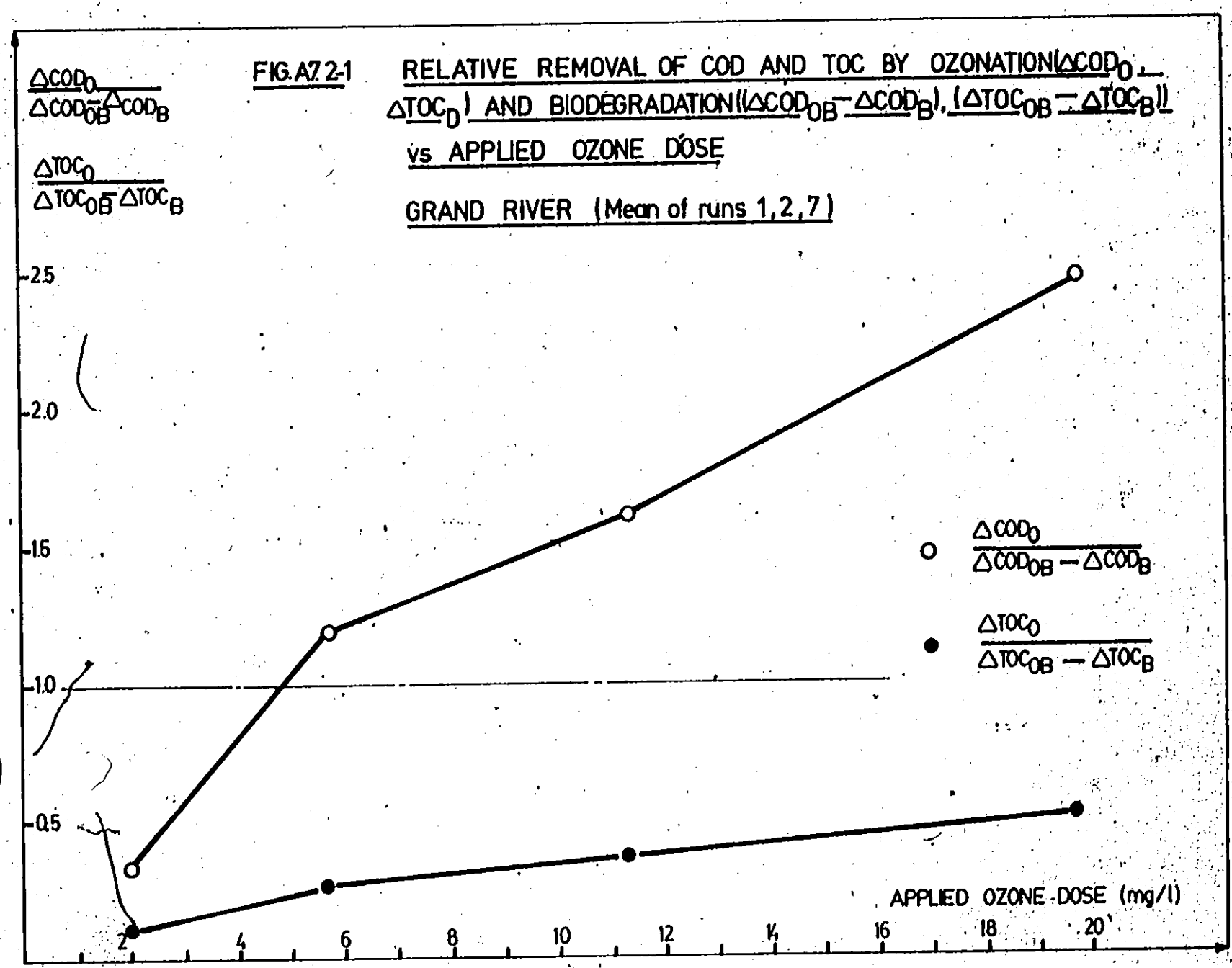


FIG.A7.2-2 RELATIVE REMOVAL OF COD AND TOC BY OZONATION (ΔCOD_O, ΔTOC_O) AND BIODEGRADATION ($\Delta COD_{OB} - \Delta COD_B$, $\Delta TOC_{OB} - \Delta TOC_B$) vs APPLIED OZONE DOSE. — SPENCER CREEK (Mean of runs 8,9.)

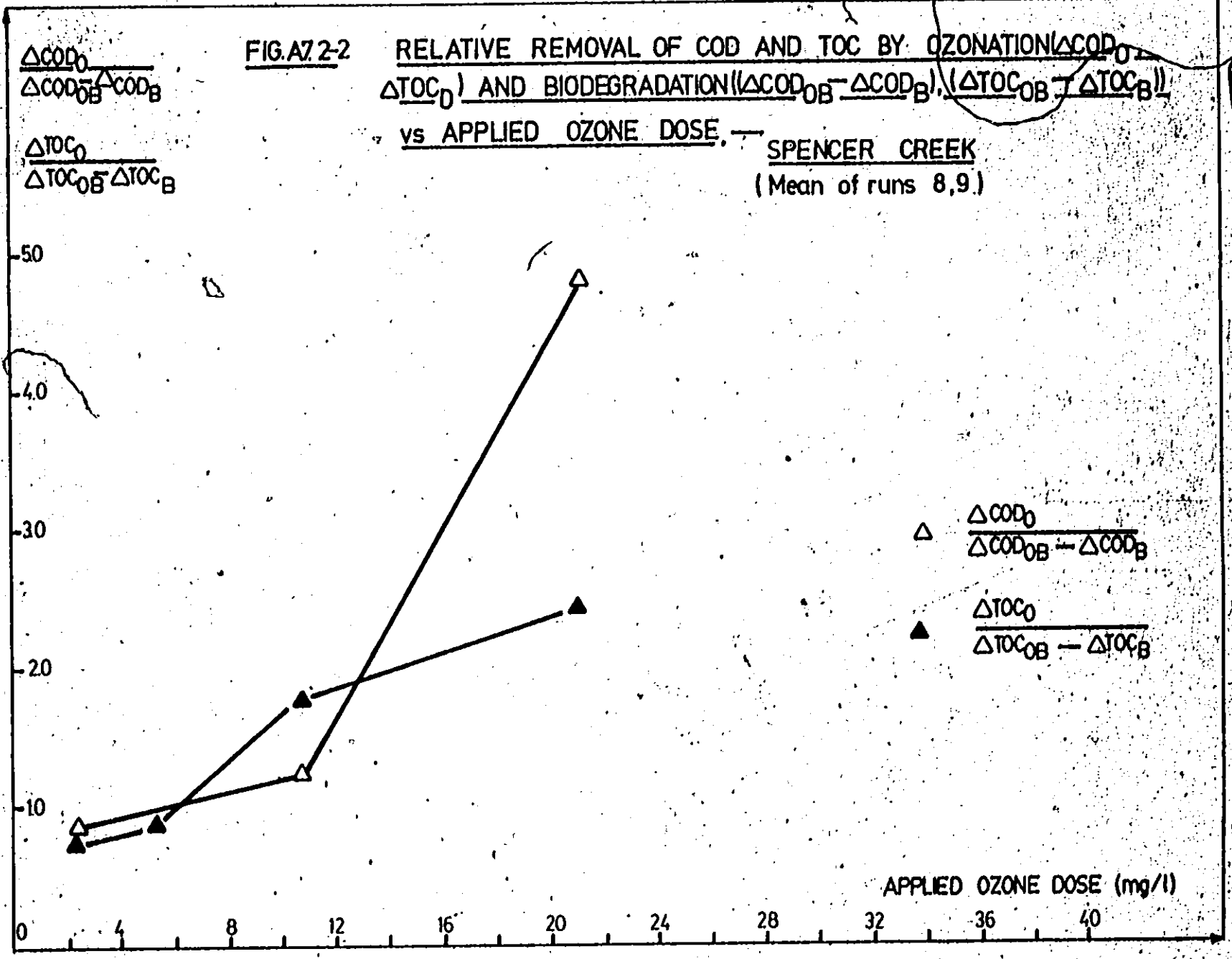
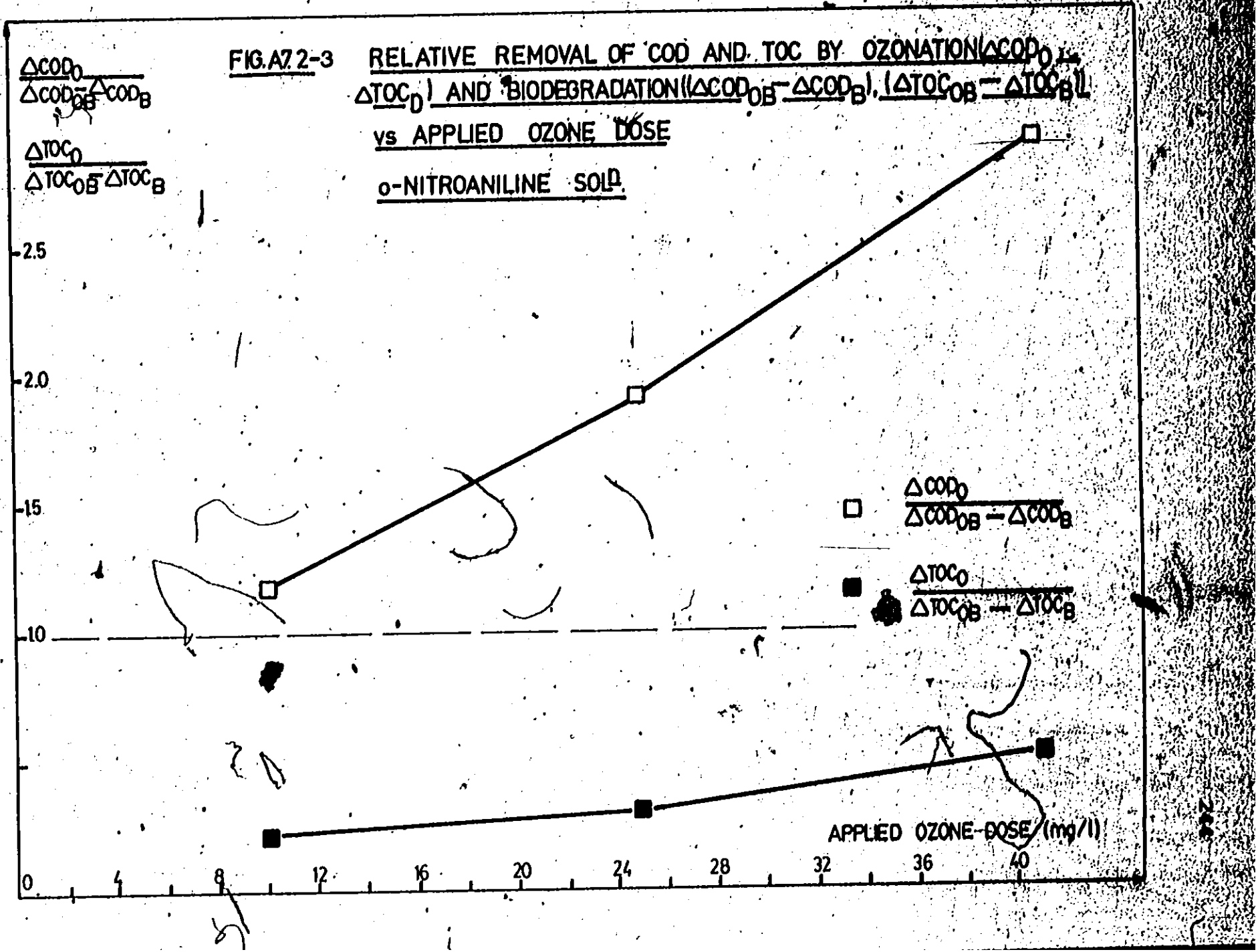


FIG. A7.2-3 RELATIVE REMOVAL OF COD AND TOC BY OZONATION (ΔCOD_O / ($\Delta COD_{OB} - \Delta COD_B$), ΔTOC_O / ($\Delta TOC_{OB} - \Delta TOC_B$)) AND BIODEGRADATION (($\Delta COD_{OB} - \Delta COD_B$) / ΔCOD_O, ($\Delta TOC_{OB} - \Delta TOC_B$) / ΔTOC_O) vs APPLIED OZONE DOSE

o-NITROANILINE SOLN.



APPENDIX 8

RAW DATA

A8.1 Soluble Organic and Inorganic Characteristics after Ozonation and Biodegradation

A8.2 Oxygen Uptake Per Respirometer (mg O_2)

APPENDIX 8 RAW DATA

A8.1 SOLUBLE ORGANIC AND INORGANIC CHARACTERISTICS AFTER OZONATION AND BIODEGRADATION

TABLE A8.1-1 GRAND RIVER WATER

Run No.	Contact Time (min)	Ozone Dose (mg/ℓ)	TOC_O[a] (mg/ℓ)	TOC_{OB} (mg/ℓ)	UV_O 254nm 10cm	UV_{OB} 254nm 10cm	COD_O (mg/ℓ)	COD_{OB} (mg/ℓ)	pH_O	pH_{OB}	TKN_O[b] (mg/ℓ)	TKN_{OB} (mg/ℓ)	NH_3-N_O (mg/ℓ)	NH_3-N_{OB} (mg/ℓ)	NO_3-N_O (mg/ℓ)	NO_3-N_{OB} (mg/ℓ)	NO_2-N_O (mg/ℓ)	NO_2-N_{OB} (mg/ℓ)
1	0.0	0.0	6.15	6.27	1.246	1.050	11.5	11.9	8.4	-	-	0.88	-	0.07	-	2.57	-	0.06
	3.5	2.1	6.05	3.68	0.824	0.755	11.2	6.7	-	-	-	0.56	-	0.00	-	2.58	-	0.05
	10.0	5.7	5.95	3.36	0.674	0.566	10.3	5.5	-	-	-	0.38	-	0.00	-	2.55	-	0.00
	20.0	11.4	5.62	2.69	0.526	0.420	9.9	4.5	-	-	-	0.20	-	0.00	-	2.80	-	0.00
	35.0	20.1	5.34	2.42	0.414	0.343	7.4	3.5	-	-	-	0.24	-	0.00	-	2.80	-	0.00
	Blank	0.0	0.41	0.46	0.094	0.097	0.0	0.1	-	-		0.30		0.18	-	0.42	-	0.03
2	0.0	0.0	5.48	6.22	1.146	1.042	10.7	9.4	8.3	8.4	-	-	-	-	-	-	-	-
	3.5	1.9	5.36	4.06	0.807	0.780	10.5	7.5	8.3	8.3	-	-	-	-	-	-	-	-
	10.0	5.5	5.10	4.03	0.580	0.545	8.1	6.8	8.3	8.6	-	-	-	-	-	-	-	-
	20.0	10.7	4.64	3.23	0.441	0.452	7.0	6.0	8.2	8.6	-	-	-	-	-	-	-	-
	35.0	19.0	4.28	3.28	0.348	0.350	7.0	4.9	7.7	8.5	-	-	-	-	-	-	-	-
	Blank	0.0	0.14	0.70	0.069	0.136	0.0	1.0	6.5	6.5	-	-	-	-	-	-	-	-
3	0.0	0.0	-	3.40	1.000	0.984	11.7	11.5	8.3	8.2	1.36	0.54	0.58	0.02	1.70	1.80	0.00	0.69
	3.5	2.0	-	3.08	0.663	0.649	9.8	9.6	8.3	8.3	1.34	1.04	0.58	0.57	1.75	1.73	0.00	0.00
	10.0	5.5	3.91	2.58	0.467	0.448	8.5	7.2	8.2	8.3	1.20	1.06	0.58	0.58	1.75	1.78	0.00	0.00
	20.0	10.6	3.66	2.18	0.356	0.358	8.3	5.2	8.1	8.2	1.14	0.81	0.57	0.58	1.83	1.78	0.00	0.00
	35.0	18.7	3.26	1.81	0.284	0.286	7.8	4.3	8.0	8.2	1.05	0.66	0.55	0.54	1.75	1.38	0.00	0.37
	Blank	0.0	0.78	0.24	0.071	0.086	0.0	0.7	7.6	7.5	0.90	0.24	0.53	0.12	0.10	0.08	0.00	0.41
4	0.0	0.0	3.66	3.83	1.083	1.062	10.7	9.2	8.4	8.5	0.96	-	0.42	-	2.23	1.94	0.00	0.13
	3.5	1.9	3.53	3.38	0.772	0.760	8.8	7.5	8.4	8.4	0.84	-	0.36	-	2.11	2.10	0.00	0.00
	20.0	11.2	2.90	2.36	0.406	0.408	6.9	5.2	8.2	8.3	0.52	-	0.38	-	2.29	2.25	0.00	0.00
	20.0[c]	11.5	2.91	2.41	0.406	0.397	7.0	5.5	8.2	8.3	0.20	-	0.03	-	1.91	2.28	0.00	0.00
	35.0	20.0	2.52	1.82	0.310	0.336	6.4	3.7	8.2	8.3	0.52	-	0.39	-	2.38	2.14	0.00	0.03
	Blank	0.0	0.24	0.35	0.068	0.098	0.0	0.2	7.9	8.0	0.66	-	0.48	-	0.22	0.18	0.00	0.35
5	0.0	0.0	6.69	6.53	1.860	1.840	12.7	12.0	8.4	8.5		-	-	-	-	-	-	-
	3.5	2.0	6.22	6.18	1.620	1.570	10.9	10.5	8.5	8.6		-	-	-	-	-	-	-
	20.0	12.0	4.87	4.31	0.922	0.866	5.8	4.0	8.3	8.5		-	-	-	-	-	-	-

TABLE A8.1-1 Cont'd

Run No.	Contact Time (min)	Ozone Dose (mg/l)	TOC_O[a] (mg/l)	TOC_{OB} (mg/l)	UV_O 254Nm 10cm	UV_{OB} 254Nm 10cm	COD_O (mg/l)	COD_{OB} (mg/l)	pH_O	pH_{OB}	TKN_O[b] (mg/l)	TKN_{OB} (mg/l)	NH_3-N_O (mg/l)	NH_3-N_{OB} (mg/l)	NO_3-N_O (mg/l)	NO_3-N_{OB} (mg/l)	NO_2-N_O (mg/l)	NO_2-N_{OB} (mg/l)
6	0.0	0.0	4.64	4.50	1.224	1.234	10.2	7.6	8.3	8.6	-	-	-	-	-	-	-	-
	3.5	2.0	4.41	4.28	1.030	1.033	7.6	6.9	8.3	8.5	-	-	-	-	-	-	-	-
	20.0	12.0	3.01	2.55	0.460	0.446	4.0	2.5	8.1	8.4	-	-	-	-	-	-	-	-
7	0.0	0.0	3.15	3.09	0.894	0.855	7.3	7.3[d]	8.3	8.3	-	-	-	-	-	-	-	-
	3.5	2.0	2.82	2.78	0.752	0.718	5.5	5.2	8.3	8.4	-	-	-	-	-	-	-	-
	10.0	6.0	2.48	2.36	0.443	0.430	4.1	3.4	8.2	8.4	-	-	-	-	-	-	-	-
	20.0	12.0	2.39	1.91	0.328	0.275	2.9	2.3	8.0	8.4	-	-	-	-	-	-	-	-
	35.0	20.0	2.21	1.45	0.217	0.270	2.2	2.0	7.9	8.4	-	-	-	-	-	-	-	-

[a]Subscripts 'O' and 'OB' refer to parameter measurement after ozonation and ozonation followed by Biodegradation respectively.

[b]All Nitrogen analyses were performed after the addition of nutrients and inoculum.

[c]No nutrient addition.

[d]Estimated data point.

TABLE 8.1-2

SPENCER CREEK WATER

Run No.	Contact Time (min)	Ozone Dose (mg/ℓ)	TOC_O (mg/ℓ)	TOC_{OB} (mg/ℓ)	UV_O[a] 254 nm 10 cm	UV_{OB}[a] 254 nm 10 cm	COD_O (mg/ℓ)	COD_{OB} (mg/ℓ)	pH_O	pH_{OB}	TKN_O[b] (mg/ℓ)	TKN_{OB} (mg/ℓ)	NH_3-N_O (mg/ℓ)	NH_3-N_{OB} (mg/ℓ)	NO_3-N_O (mg/ℓ)	NO_3-N_{OB} (mg/ℓ)	NO_2-N_O (mg/ℓ)	NO_2-N_{OB} (mg/ℓ)
8	0.0	0.0	9.20	8.10	0.455	0.437	22.6	19.6	8.7	8.5	1.46	0.56	-	-	0.46	1.06	0.00	0.00
	3.5	2.3	8.88	7.34	0.392	0.362	21.3	15.5	8.6	8.3	1.40	0.56	-	-	0.58	0.44	0.00	0.88
	17.5	10.6	7.55	5.68	1.000	1.560	17.9	12.7	8.4	8.3	1.40	0.45	-	-	0.70	0.67	0.00	0.85
	70.0	40.0	4.57	3.17	0.702	0.648	9.1	7.3	8.2	8.2	1.22	0.25	-	-	0.80	1.58	0.00	0.00
	Blank	0.0	0.21	0.20	0.086	0.091	0.0	0.7	7.5	6.1	0.84	0.02	-	-	0.33	1.04	0.00	0.00
9	0.0	0.0	8.03	7.56	0.417	0.399	16.0	16.0	8.6	8.8	-	-	-	-	0.63	0.56	0.00	0.00
	3.5	2.1	7.67	6.75	0.356	0.326	14.2	13.5	8.5	8.7	-	-	-	-	0.68	0.61	0.00	0.00
	8.5	5.1	7.37	6.01	1.950	1.765	12.8	11.3	8.5	8.6	-	-	-	-	0.70	0.64	0.00	0.00
	35.0	21.0	5.60	4.01	1.126	0.994	9.1	6.2	8.2	8.6	-	-	-	-	0.80	0.75	0.00	0.00
	Blank	0.0	0.42	0.77	0.071	0.113	0.0	0.8	7.4	8.3	-	-	-	-	0.68	1.22	0.00	0.00

TABLE 8.1-3

AQUEOUS NITROANILINE SOLUTIONS

Run No.	Contact Time (min)	Ozone Dose (mg/ℓ)	TOC_O (mg/ℓ)	TOC_{OB} (mg/ℓ)	UV_O[c] 254 nm 10 cm	UV_{OB}[c] 254 nm 10 cm	COD_O (mg/ℓ)	COD_{OB} (mg/ℓ)	pH_O	pH_{OB}	TKN_O[b] (mg/ℓ)	TKN_{OB} (mg/ℓ)	NH_3-N_O (mg/ℓ)	NH_3-N_{OB} (mg/ℓ)	NO_3-N_O (mg/ℓ)	NO_3-N_{OB} (mg/ℓ)	NO_2-N_O (mg/ℓ)	NO_2-N_{OB} (mg/ℓ)
10[d]	0.0	0.0	9.69	3.05	0.483	0.300	31.1	10.0	8.1	7.3	2.66	-	0.98	-	0.18	0.05	0.00	1.75
	3.5	1.9	9.63	9.72	0.499	0.478	30.4	29.7	8.1	8.2	3.52	-	1.09	-	0.23	0.05	0.07	0.13
	17.5	9.6	8.88	7.74	0.504	0.436	24.8	21.9	8.1	8.1	3.36	-	1.35	-	0.56	0.10	0.20	0.37
	45.0	25.6	7.88	4.38	0.365	0.295	20.0	11.5	8.1	8.0	2.94	-	1.60	-	1.35	0.97	0.12	0.23
	Blank	0.0	0.24	0.32	0.068	0.095	0.0	1.1	7.9	8.0	0.92	-	-	-	0.00	0.0	0.00	0.75
11[e]	0.0	0.0	10.85	10.81	0.738	-	30.6	32.9	8.3	8.5	-	-	-	-	0.33	0.35	0.00	0.00
	17.5	10.0	10.42	8.39	0.722	-	24.7	22.1	7.7	8.1	-	-	-	-	0.73	1.57	0.13	0.31
	45.0	25.0	9.58	5.35	0.535	-	19.2	15.6	7.4	7.7	-	-	-	-	1.63	3.31	0.10	0.42
	70.0	41.2	8.11	2.82	0.293	-	11.4	7.1	7.2	8.0	-	-	-	-	2.32	4.17	0.04	0.36
	Blank	0.0	0.42	0.40	0.071	-	0.0	0.8	7.4	8.4	-	-	-	-	0.43	1.13	0.00	0.00

[a] For ozone contact times of 0.0, 3.5, and 8.5 mins. samples were diluted 10:1 with the blank prior to determining the absorbance

[b] All Nitrogen Analyses were performed after the addition of nutrients and inoculum.

[c] All samples excepting the blank were diluted 10:1 with the blank prior to determining the absorbance.

[d] p-Nitroaniline (para)

[e] o-Nitroaniline (ortho)

A8.2 OXYGEN UPTAKE PER RESPIROMETER (mg O_2)

TABLE A8.2-1 GRAND RIVER WATER, RUN 3

Ozone Contact (min)	Resp. Vol. (ℓ)	Incubation Time (days)														
		0.9	2.0	3.1	3.9	5.0	5.9	7.1	7.9	9.1	10.0	10.9	11.9	13.1	14.0	15.1
0.0	9.85	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.0	1.0	1.0	2.4	7.0	12.8
3.5	9.80	0.8	0.8	1.3	1.9	1.9	3.8	5.6	5.9	8.4	8.4	8.4	8.4	12.3	14.7	14.7
10.0	9.77	1.0	1.0	2.3	3.8	4.1	7.1	9.1	9.3	12.3	12.3	13.1	13.8	15.1	15.8	15.8
10.0	9.82	0.1	0.1	0.5	1.3	1.3	3.8	5.8	6.1	9.0	9.0	9.0	9.0	13.4	15.9	15.9
10.0[a]	9.78	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.6	5.4	7.0
10.0[a]	9.80	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.9	6.5	8.1
20.0	9.73	2.3	2.3	2.3	2.8	2.8	4.8	6.6	6.6	9.3	9.3	9.3	9.3	13.0	15.6	15.6
35.0	9.86	0.5	0.5	1.3	3.3	3.7	6.7	9.3	9.3	12.6	12.6	12.6	12.6	15.6	18.5	18.5
35.0	9.89	0.0	0.0	0.4	1.9	2.4	5.1	7.6	7.6	10.6	10.6	10.6	10.6	14.0	16.6	16.6
Blank	9.65	0.0	0.0	0.0	0.0	0.0	0.5	0.5	0.5	2.0	2.5	2.5	2.5	3.6	6.6	9.3
				(75.8[b])(74.8)			(75.2)(75.3)(74.9)				(75.1)(74.2)(74.3)				(75.8)(74.8)	

TABLE A8.2-2 GRAND RIVER WATER - RUN 4

Ozone Contact (min)	Resp. Vol. (ℓ)	Nutr.[c]	Incubation Time (days)							
			1.2	2.0	3.2	4.0	5.3	6.0	7.0	8.0
0.0	9.77	Yes	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3.5	9.90	Yes	0.0	0.0	2.0	5.1	9.1	9.1	9.1	9.1
3.5	9.86	Yes	0.0	0.0	3.6	7.2	12.1	12.1	12.1	12.7
20.0	9.80	Yes	0.0	0.0	4.8	8.1	12.5	12.5	12.5	14.3
20.0	9.76	Yes	0.0	0.0	2.2	4.5	8.1	8.1	8.1	8.5
20.0	9.80	No	1.8	1.8	3.6	6.1	9.2	9.2	9.2	9.2
20.0	9.85	No	1.1	1.1	4.4	7.9	12.8	12.8	12.8	14.4
35.0	9.80	Yes	0.0	0.0	0.5	4.4	9.8	11.9	11.9	15.5
Blank (73.8)[b]	9.80	Yes	0.0 (73.8)	0.0	0.0 (74.0)	0.0 (74.7)	1.6 (75.6)	3.5 (74.8)	4.1 (74.1)	4.1 (75.1)

[a]Sample ozonated at pH 3.0 and adjusted to pH 8.3 with H_2SO_4 prior to biodegradation.

[b]Atmospheric pressure (cm Hg)

[c]Nutrients all other runs unless otherwise stated.

TABLE A8.2-3 GRAND RIVER WATER - RUNS 5,6,7

Ozone Contact (min)	Resp. Vol. (ℓ)	Incubation Time (days)													
		1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	12.0	13.0	16.0	17.0
Run 5															
0.0	9.85	0.0	0.4	1.6	2.0	2.0	3.1	8.2	11.7	12.9	17.7	23.2	25.8	30.2	30.6
3.5	9.73	0.0	0.8	1.1	1.1	1.1	1.7	7.6	12.3	13.8	18.8	25.5	28.2	31.8	31.8
3.5	9.86	0.0	0.0	0.0	0.0	0.0	2.3	9.2	14.1	15.1	19.7	26.3	29.0	33.7	33.7
20.0	9.80	0.0	0.6	0.6	0.6	0.6	0.6	5.8	10.2	10.2	13.8	22.8	25.7	31.5	32.1
20.0	9.90	0.0	0.0	0.6	1.2	1.8	3.8	9.7	15.1	15.1	16.6	23.2	25.7	28.3	28.3
Run 6															
0.0	9.80	0.0	0.6	0.6	0.6	0.6	0.6	3.2	5.3	5.3	5.3	10.5	11.9	15.2	15.2
3.5	9.77	0.0	1.5	2.0	2.5	2.9		9.3	10.5	10.5	10.5	15.8	17.2	19.7	19.7
3.5	9.89	0.1	1.6	1.6	2.1	2.6	3.6	8.4	11.8	11.8	11.8	17.4	19.2	21.3	22.1
20.0	9.80	0.1	0.1	0.1	0.1	0.1	2.6	9.9	14.1	15.0	15.4	20.2	21.8	24.1	24.1
20.0	9.85	0.2	0.5	0.8	1.1	1.1	2.6	8.4	12.7	12.7	13.4	19.4	21.8	28.5	28.9
Blank	9.80	0.0	1.2	4.7	7.9	10.5	14.0	20.4	24.2	24.2	25.2	28.2	28.7	31.2	31.7
(76.2)[a]		(76.4)	(75.8)	(75.4)	(75.7)	(75.4)	(76.6)	(77.6)	(76.7)	(76.8)	(75.9)	(76.2)			
Run 7															
0.0	9.73	0.0	0.3	0.3	0.3	0.3	0.3	4.0	7.6	11.2	13.7	16.6	22.6	27.8	
3.5	9.80	0.0	0.0	0.0	0.0	0.0	0.0	2.6	7.2	10.3	13.5	15.8	21.9	25.6	
10.0	9.77	0.0	1.0	1.0	1.0	1.0	1.0	6.8	10.9	13.4	16.2	17.8	23.4	28.3	
20.0	9.86	0.0	3.5	3.5	4.7	4.7	6.3	12.5	16.0	18.8	20.1	20.9	26.4	32.0	
35.0	9.85	0.0	2.8	2.8	4.1	4.1	7.6	13.0	16.0	18.3	19.4	20.2	24.8	30.2	
Blank	9.89	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.0	3.3	3.7	3.7	7.6	8.2	

[a]Atmospheric pressure.

TABLE A8.2-4 SPENCER CREEK, RUN 8

Ozone Contact (min)	Resp. Vol. (ℓ)	Incubation Time (days)													
		0.5	2.4	3.4	5.5	7.4	8.4	9.4	12.4	13.5	15.6	17.6	18.5	20.4	24.6
0.0	9.77	0.1	13.1	13.1	14.6	14.6	14.6	14.6	14.6	14.6	14.6	16.9	18.6	18.6	18.6
3.5	9.90	0.1	14.4	14.9	18.7	19.7	19.7	19.7	19.7	19.7	22.6	28.4	31.2	33.5	51.0
17.5	9.85	0.6	11.3	11.3	14.5	20.0	22.6	22.9	22.9	22.9	24.6	39.0	43.2	45.2	58.7
17.5	9.80	0.1	14.7	15.9	20.5	22.9	24.5	25.0	28.5	28.5	44.9	53.9	55.3	55.3	69.5
70.0	9.85	0.5	15.6	17.5	23.4	28.8	30.2	30.6	31.5	31.5	34.7	45.0	48.8	51.2	70.2
70.0	9.80	0.1	10.5	11.5	16.1	20.7	23.7	24.1	26.0	26.0	30.2	38.0	42.8	47.8	65.7
Blank	9.85	0.0	9.7	9.7	9.7	9.7	9.7	9.7	12.9	12.9	21.5	25.4	26.9	26.9	33.7

TABLE A8.2-5 SPENCER CREEK, RUN 9

Ozone Contact (min)	Resp. Vol. (ℓ)	Incubation Time (days)													
		0.5	2.4	3.5	5.3	7.4	8.5	9.5	12.5	14.2	15.2	18.2	19.3	21.2	24.3
0.0	9.90	1.1	3.0	3.0	3.0	3.0	3.7	3.7	3.7	4.9	6.1	6.1	7.2	10.3	10.3
3.5	9.85	2.3	5.3	5.9	5.9	5.9	10.0	10.0	10.0	14.0	15.3	15.3	18.3	22.9	22.9
3.5	9.90	1.0	1.0	1.0	1.0	1.0	1.0	3.6	3.6	5.2	7.7	7.7	11.2	15.8	15.8
8.5	9.20	1.5	1.5	2.0	2.0	2.6	5.5	5.5	5.5	10.8	12.8	12.8	12.8	16.1	16.1
8.5	9.78	1.4	2.9	3.4	3.4	4.7	8.7	8.7	8.7	10.5	12.8	13.3	18.2	23.4	26.2
Blank	9.90	0.0	0.0	0.0	0.0	0.0	3.4	3.4	3.4	3.4	5.1	5.1	7.7	9.2	9.7
(76.1)[a]		(76.6)	(75.4)	(74.8)	(75.9)	(76.5)	(75.8)	(75.3)	(76.7)	(76.2)	(75.0)	(76.8)	(76.2)	(76.4)	(74.6)

[a]Atmospheric pressure (cm Hg)

TABLE A8.2-6

p-NITROANILINE SOLUTION, RUN 10

Ozone Dose (mg/ℓ)	Resp. Vol. (ℓ)	Incubation Time (days)												
		1.0	2.0	3.4	4.2	5.1	6.2	7.1	8.2	9.1	10.3	11.1	12.1	13.1
0.0	9.85	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	11.5	21.3	41.8	74.0
1.9	9.90	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1.9	9.65	0.0	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.6
9.6	9.93	0.0	0.0	0.0	0.0	0.0	1.2	2.3	2.3	3.5	7.0	7.9	8.6	11.9
9.6	9.12	1.8	2.8	2.8	2.9	4.0	8.3	9.3	9.3	11.2	15.3	15.8	15.8	16.6
25.6	9.90	0.0	0.0	0.5	4.5	8.4	11.7	14.7	16.4	20.5	26.9	29.2	30.4	35.0
25.6	9.82	1.0	2.4	7.4	12.7	15.5	17.0	21.7	25.1	32.0	41.0	43.3	45.1	49.3
Blank (76.0)[a]	9.78	0.0 (74.7)	0.0 (74.7)	0.0 (74.8)	0.0 (75.2)	0.0 (75.3)	0.0 (75.4)	0.0 (73.3)	0.0 (74.0)	0.0 (74.7)	1.5 (75.6)	5.7 (74.8)	8.8 (74.1)	14.8 (75.1)

TABLE A8.2-7

o-NITROANILINE SOLUTION, RUN 11

Ozone Dose (mg/ℓ)	Resp. Vol. (ℓ)	Incubation Time (days)																				
		0.5	1.6	2.4	3.5	4.5	5.3	6.5	7.4	8.5	9.5	11.3	12.5	14.2	15.2	16.3	18.2	19.3	21.2	22.2	24.3	29.4	32.5
0.0	9.85	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.2	3.4	3.4	3.4	3.4	3.4
10.0	9.77	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.8	5.3	5.3	5.3	13.7	16.1	16.1	16.1	18.4	23.7	24.7	24.7	26.9	46.7
10.0	9.85	0.4	0.4	1.2	2.3	2.3	2.3	6.3	6.3	12.6	12.6	12.6	12.6	21.2	23.9	23.9	23.9	28.9	32.4	32.9	32.9	34.1	34.5
25.0	9.80	0.0	0.0	3.3	7.8	9.1	11.6	21.7	23.5	34.3	36.2	39.0	40.6	51.2	53.4	53.4	53.4	57.1	65.2	67.4	96.4	117.6	120.8
25.0	9.82	0.6	2.5	4.1	8.8	10.0	13.3	23.0	24.5	35.1	37.2	39.2	41.6	52.1	55.3	55.7	55.7	59.8	65.0	65.5	65.5	98.8	104.6
41.2	9.77	0.0	0.0	0.0	2.35	3.0	5.3	13.8	15.6	28.4	31.5	34.6	37.5	50.8	56.9	62.7	85.7	100.7	118.3	120.5	125.5	131.6	135.2
41.2	9.73	0.7	1.3	2.6	8.8	10.7	13.7	22.2		34.5	36.9	39.7	42.9	55.0	59.3	60.9	78.5	95.3	117.1	121.5	132.3	141.5	141.6
Blank (76.1)[a]	9.80	0.0 (76.6)	0.0 (76.1)	0.0 (75.4)	0.0 (74.8)	0.0 (74.9)	0.0 (75.9)	0.0 (76.3)	0.0 (76.5)	4.7 (75.8)	6.5 (75.3)	12.7 (75.7)	16.3 (75.7)	28.6 (76.2)	31.0 (75.0)	31.0 (76.0)	31.0 (76.8)	33.9 (76.2)	40.7 (76.4)	40.7 (74.3)	41.2 (74.5)	44.6 (74.6)	44.6 (75.0)

[a]Atmospheric pressure (cm Hg)