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PHOTODEGRADATION OF THE  
DYESTUFF DISPERSE BLUE 26 IN WATER

by

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## ABSTRACT

The photodegradation of the dyestuff Disperse Blue 26 has been studied in sunlight and under 300 nm light in organic-free water and in natural waters. Dissolved humic acid has been demonstrated to promote the photodecomposition of the dye. The results indicate that the half-life of sunlight degradation of the dye in near-surface waters will be of the order of a few days in summer to a few weeks in winter. Moreover, photolysis will be retarded at depths greater than a few decimetres to two metres, and may be retarded by the predicted slight tendency of Disperse Blue 26 to partition to sediment.

## RÉSUMÉ

La photolyse du colorant Disperse Blue 26 dans une eau ne contenant aucune matière organique et dans une eau naturelle, a été étudiée sous éclairage solaire et sous une lumière à 300 nm. Il a été montré que l'acide humique dissous accélère la photolyse du colorant. Les résultats montrent que la demi-vie du colorant dans la tranche superficielle d'eau exposée à la lumière du soleil est de l'ordre de quelques jours l'été à quelques semaines l'hiver. En outre, la photolyse se trouve retardée lorsque le colorant se trouve à une profondeur comprise entre quelques décimètres et deux mètres; elle peut être retardée par la légère tendance prévue du Disperse Blue 26 à passer dans les sédiments.

## MANAGEMENT PERSPECTIVE

Dyestuffs are high volume chemicals which may enter aquatic environments in significant quantities. Interest in the environmental behaviour of dyestuffs arose largely from concerns about carcinogenicity. Very little is known of the environmental occurrence, persistence and fate of dyes. Disperse Blue 26 is a popular disperse dye which is used in the Eastern Townships of Quebec, an area in which many of Canada's textile mills and carpet dyeing operations are located.

The photodegradation of the dyestuff Disperse Blue 26 has been studied in sunlight and under 300 nm light in organic-free water and in natural waters. Dissolved humic acid has been demonstrated to promote the photodecomposition of the dye. The results indicate that the half-life of sunlight degradation of the dye in near-surface waters will be of the order of a few days in summer to a few weeks in winter. Moreover, photolysis will be retarded at depths greater than few decimetres to two metres, and may be retarded by the predicted slight tendency of Disperse Blue 26 to partition to sediment.

## PERSPECTIVE-GESTION

Les colorants sont des produits chimiques utilisés en grand volume qui peuvent atteindre le milieu aquatique en quantité importante. L'intérêt pour le comportement des colorants dans le milieu est largement issu des craintes de carcinogénéicité de ces produits. On connaît très peu de choses sur la présence, la persistance et le sort des colorants dans le milieu. Le Disperse Blue 26 est un colorant photosoluble populaire qui est utilisé dans les Cantons de l'Est, Québec, c'est-à-dire dans un secteur où sont regroupées de nombreuses usines de textile et des installations de teinture des tapis.

La photolyse du colorant Disperse Blue 26 dans une eau ne contenant aucune matière organique et dans une eau naturelle, a été étudiée sous éclairage solaire et sous une lumière à 300 nm. Il a été montré que l'acide humique dissous accélère la photolyse du colorant. Les résultats montrent que la demi-vie du colorant dans la tranche superficielle d'eau exposée à la lumière du soleil est de l'ordre de quelques jours l'été à quelques semaines l'hiver. En outre, la photolyse se trouve retardée lorsque le colorant se trouve à une profondeur comprise entre quelques décimètres et deux mètres; elle peut être retardée par la légère tendance prévue du Disperse Blue 26 à passer dans les sédiments.

## INTRODUCTION

Man has used dyes for at least a few thousand years, and today the chemistry of dyes and dyeing processes has very great technical importance. Alizarin, extracted as the glycoside rubierythric acid from madder, was used by the ancient Egyptians and Persians (1). The use of indigo dates back to 3000 B.C., and Tyrian Purple, prepared from a sea snail, has been used since the Roman era. In 1856, Perkin prepared the first synthetic dyestuff, mauveine (1). Early important applications of synthetic organic chemistry were largely in the field of dyestuffs.

The distinction between dyes and pigments is largely made on the basis of solubility. Pigments have extremely low solubility in water, and are not very soluble in organic solvents either, generally being applied in the solid state. Dyes are generally more soluble either in water or organic solvents.

Dyes are classified according to both chemical structure and type of application. Chemical classes include azo, stilbene, di- and triphenylmethane, xanthene, acridine, quinoline, methine, azine, oxazine, thiazine, sulfur, anthraquinone, indigoid, and phthalocyanine moieties. Application types include acidic, basic, direct, disperse, mordant, reactive, sulfur, and vat dyes. Table 1 describes the applications of various dyes. Dyes are classified in the Colour Index (2), which lists 8000 different active ingredients and many more formulations. The classification includes the application type, the colour

and a five digit number (e.g., Disperse Blue 26, C.I. No. 63305). In addition, each dye, like any other chemical, has a Chemical Abstracts Service number. Dyestuffs are large volume industrial chemicals. Global production in 1978 was estimated to be  $6.4 \times 10^8$  kg of active ingredient (1). About  $10^8$  kg were produced in the United States in 1986 (3). It has been estimated that 90% of dyes applied end up in fabrics, with the remaining 10% discharged to waste streams (4).

Interest in the environmental behaviour of dyes arose largely from concerns about carcinogenicity. Some dyes are carcinogens (5), and others after transformation yield compounds such as aromatic amines which may be carcinogenic or otherwise toxic (e.g., ref. 6). Very little is known of the environmental occurrence, persistence and fate of dyes. Disperse dyes (a widely used class - ref. 7) are of particular interest since they are neutral compounds of very low water solubility, hence they may concentrate in sediments and biota. Since they are designed to resist oxidation (e.g., by bleach), they may resist aerobic degradation. Vapour pressures of disperse dyes tend to be low, hence volatilization is probably not important (8). Such dyes may degrade as a result of sunlight photolysis, anaerobic degradation or some combination of photolysis and aerobic or anaerobic degradation. It has been shown that some less water-soluble disperse, vat and sulfur dyes photodegrade considerably more slowly than the more water-soluble basic, acidic and direct dyes (4). This article reports the kinetics of photodegradation of Disperse Blue 26 in pure water and natural water. Disperse Blue 26, a popular disperse dye, is used in

the Eastern Townships of Quebec (9), an area in which many of Canada's textile mills and carpet dyeing operations are located. Figure 1 shows the structure of Disperse Blue 26, and Table 2 shows some of its properties.

## EXPERIMENTAL SECTION

### Materials

Technical grade Disperse Blue 26 was obtained from E.A. Clarke of the Ecological and Toxicological Association of the Dyestuffs Manufacturing Institute (Washington, DC, USA). Humic acid was from Aldrich (Milwaukee, WI, USA). Pesticide grade organic solvents were obtained from different suppliers and their purity (at 1000X concentration) was checked before use. The sodium sulfate, aluminum foil, glass fibre filters and disposable pipets were heated to 500°C for 24 h before use. All glassware was rinsed with pesticide grade solvents before use. Organic-free water was obtained from a Milli-Q system (Millipore, Mississauga, Ontario, Canada) which consisted of a reverse osmosis filter followed by two ion-exchange columns and an activated charcoal column, followed by filtration through a 0.22 µm filter. Natural water used in this work was first filtered through a 0.45 µm filter. Samples of natural water were collected from Hamilton Harbour on Lake Ontario, the Grand River in Ontario, and the Yamaska River in the Eastern Townships of Quebec.



## Methods

Ultraviolet-visible spectra were recorded with a Shimadzu UV-260 spectrophotometer (Tekscience, Oakville, Ontario, Canada). The purity of the Disperse Blue 26 sample was checked with a Waters Associates (Millipore-Waters, Mississauga, Ontario, Canada) high performance liquid chromatograph and 990+ diode array spectrophotometric detector. The sample was applied to a 15 cm x 4.6 mm i.d. Waters Associates NovaPak reverse phase C<sub>18</sub> column, with a linear gradient from 100% water to 100% methanol in 15 minutes, and flow rate 1.5 mL/min.

Ultraviolet photolysis experiments were conducted with a Rayonet photochemical reactor (Southern New England Ultraviolet Co., Hamden, CT, USA) and 20 mm o.d. x 300 mm long capped EXAX tubes (Fisher Scientific Co., Unionville, Ontario, Canada). The photoreactor was equipped with fluorescent-coated Hg lamps with peak intensity at 300 nm (RPR-3000A) and 30 nm half-bandwidth. Solutions were not deaerated. The temperature was 36 ± 2°C. Samples of the photolysis solutions in organic-free water or natural water were periodically withdrawn for spectrophotometric analysis. Appropriate dark controls were used in all cases. Light intensity ( $I_{\lambda}$ ) was determined by the ferrioxalate actinometric method of Hatchard and Parker (10). The photolysis quantum yield,  $\phi$ , was calculated according to the equation

$$\phi = k_p / (2.303 \times \epsilon_\lambda \times I_\lambda \times L) \quad (1)$$

where  $k_p$  is the photolysis rate constant,  $\epsilon_\lambda$  the extinction coefficient of Disperse Blue 26 at 300 nm and  $L$  the path length (11).

Sunlight photolysis experiments were conducted in Pyrex containers exposed on the roof of the laboratory in the summer and fall of 1988. Appropriate dark controls were used. Total incident global solar irradiation (langleys) was measured at a meteorological station on the same roof (latitude 44°N).

Since humic material is known to promote the photolysis of some chemicals in water (e.g., 11-13), the effects of humic acid on the laboratory and sunlight photolysis of Disperse Blue 26 were also studied.

In an effort to identify products of photolysis of Disperse Blue 26, solutions which had been exposed to 300 nm light or sunlight were extracted with methylene chloride, and the methylene chloride extracts were dried, concentration to a small volume, transferred to hexane with a toluene "keeper", and analyzed by gas chromatography with flame ionization, electron capture and mass spectral detectors, both underivatized and after derivatization with diazomethane, acetic anhydride and pentafluorobenzyl bromide. However, although it was visually apparent that Disperse Blue 26 could be photodegraded under 300 nm light or sunlight, no products were detected.

## RESULTS AND DISCUSSION

The photolysis of organic contaminants in fresh water may occur directly or indirectly, and may depend to a considerable degree on the nature and concentrations of naturally-occurring substances since these latter substances (i) may attenuate sunlight, (ii) may absorb light to produce excited states which react with other chemicals, and/or (iii) may through their own reaction with sunlight produce free radicals which can react further (e.g., hydrogen peroxide and nitrite ion) (12). Humic substances in particular have been shown to sensitize photoreactions of a variety of organic chemicals in natural waters (11-13).

Figure 2 shows the absorption spectrum of Disperse Blue 26 at a nominal concentration of 1 mg/L in organic-free water. In the visible region of the spectrum, maximal absorption was in the region 581-584 nm, and was essentially invariant with pH in the pH range 2-10.8 as shown in Table 3. The ultraviolet spectrum was compared with an average spectral distribution for sunlight (14,15), which indicated the potential for sunlight degradation. The degree of spectral overlap between the electronic absorption spectrum of a chemical and the emission spectrum of the light source is one of the primary determinants of direct photolysis rates in dilute solution. The lowest wavelength of sunlight at the earth's surface is about 290 nm. Values of  $\epsilon > 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$  for a particular compound at wavelengths greater than 290 nm indicate that the compound may be susceptible to sunlight photodegradation (15).

Figure 3 is a high performance liquid chromatogram of technical grade Disperse Blue 26 at 220 nm, indicating the presence of contaminants. None of these contaminants, however, absorbed light at wavelengths greater than 400 nm, indicating that they were not dyes. Moreover, a full-wavelength scan by the diode array detector of the Disperse Blue 26 peak showed substantially the same spectrum and absolute absorbance as the technical grade dyestuff in the spectrophotometer. This indicated that the contaminants were present in fairly small amounts - negligible for the purposes of this study.

Figure 4 shows that the kinetics of photolysis of Disperse Blue 26 in the photoreactor at 300 nm were first order in all waters examined, and that the degradation rate was faster in natural waters than in organic-free water. There was no degradation in the dark controls. The data were analyzed by the method of least squares and the results are shown in Table 4. The photodegradation half-life in organic free water was about 7 d, and about 1.4-2.3 d in natural waters, perhaps due to a photosensitized reaction or to a photoinitiated free radical process.

Figure 4 shows the kinetics of disappearance of Disperse Blue 26 in organic-free water and natural water exposed to sunlight in July 1988. There was no degradation in the dark controls. The kinetic results are shown in Table 5. The half-life was about 11 d in organic-free water, and 2-3 times shorter in natural waters. Similar experiments were carried out in September 1988, and because of the diminished sunlight intensity the half-lives of degradation in each

kind of water were about a factor of two longer. Half-lives of photolysis at 300 nm were thus about one half to one quarter of those determined for sunlight photolysis in June and September 1988, respectively.

Humic materials are known to promote the photolysis of certain chemicals in water (11-13). Table 6 shows that in general concentrations of humic acid in the range 5-40 mg/L increased the photodegradation rate of Disperse Blue 26 in sunlight and in 300 nm light.

These results indicate that the sunlight degradation of Disperse Blue 26 in near-surface waters will likely have a half-life of the order of a few days in summer to a few weeks in winter, which is in rough agreement with the results of Porter on other disperse dyes (4). Half-lives at greater depths will likely be longer. Because of the absorption of sunlight by naturally-occurring material, sunlight penetration into fresh water with concomitant photolysis is probably not important at depths greater than a few decimetres to two metres (14,16). Moreover, Disperse Blue 26 will have a slight tendency to partition to sediment (cf.  $\log K_{ow} = 1.61$  from Table 2), which may further retard sunlight degradation. Further studies are planned on the aerobic and anaerobic biodegradation of Disperse Blue 26.

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Table 1. Classes of dyestuffs.\*

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**Acid**

Water-soluble, anionic dyes used primarily on nylon, wool, silk and modified acrylic textiles. They consist of azo, anthraquinone and triarylmethane compounds with a few azine, xanthene, ketone, imine, nitro, nitroso and quinoline compounds. Acid dyes are applied in the presence of an organic or inorganic acid.

**Azoic**

Azoic dyes are used as complementary dyes with pigments or mordant dyes on cellulosic fibers. All of these dyes contain chromophoric azo groups located between aromatic systems.

**Basic**

Water-soluble, cationic dyes for application to modified acrylics, modified nylons, modified polyesters, leather, unbleached paper and inks. Acrylic, nylon and polyester fibers are modified by incorporation of acidic groups as dye sites in the fiber to increase its ability to be dyed with basic dyes. Principal chemical classes of basic dyes are azo, anthraquinone, triarylmethane, methine, thiazine, oxazine, acridine and quinoline. The dyes are applied in acidic dyebaths to fibers made of negatively charged polymer molecules.

**Direct**

Water-soluble, anionic dyes used for colouring cotton, rayon, other cellulosic fibers, leather and paper. Dyes of this class include azo and metallized azo compounds, as well as stilbenes, thiazoles, phthalocyanines and oxazines.

**Disperse**

Water-insoluble, non-ionic dyes used on polyester, nylon, cellulose diacetate, cellulose triacetate and acrylic fibers. Chemical types include azo, anthraquinone, nitro, methine and quinoline compounds. Disperse dyes are applied as aqueous dispersions, either by high-temperature pressure methods or low-temperature carrier methods.

**Fiber-reactive**

Water-soluble, anionic dyes containing a reactive group (such as dichlorotriazine, monochlorotriazine or vinylsulfone) that can form a covalent bond with a compatible group on the substrate. Such covalent groups may be formed with the hydroxyl groups of cellulosic fibers such as cotton and rayon, or with the amino groups in nylon, silk and wool.

Table 1. (cont'd)

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### Fluorescent brighteners

Colourless compounds that absorb incident ultraviolet light and re-emit in the blue region of the spectrum. Although not strictly considered as dyes, fluorescent brighteners are used in textiles as well as in soaps and detergents and add light to a substrate. The class includes stilbene, azole, coumarin, pyrazine and naphthalimide chemical types. Application is from solution, dispersion or suspension.

### Food, drug and cosmetic

Synthetic organic colourants that are subject to health certification for use in foods, drugs and cosmetics. These dyes consist of azo, anthraquinone, carotenoid and triarylmethane compounds.

### Mordant

Mainly used to dye wool, but the class has secondary applications for dyeing silk, nylon, leather and anodized aluminum. A mordant helps fix dye to the fiber in the form of a complex. Mordants contain chemical groups capable of reacting with salts of aluminum, chromium, cobalt, copper and iron to give differently coloured metal complexes.

### Solvent

Dyes used principally in lacquers, varnishes, printing inks and plastics. Chemical types include azo, triphenylmethane, anthraquinone and phthalocyanine. Solvent dyes are soluble in organic solvents, which are used to disperse the dyes in the substrate.

### Sulfur

Water-soluble dyes used on cotton, rayon and cellulosic blends with nylon, acrylic and polyester. These dyes contain sulfur both as a part of the chromophore and in polysulfide pendant chains.

### Vat

Water-insoluble dyes applied in dispersions used principally for dyeing and printing cotton. Chemical classes of vat dyes include anthraquinones and indigoids.

Table 2. Disperse Blue 26.

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Chemical Abstracts Service No. 3860-63-7

Colour Index No. 63305

Chemical Name: 1,5-di(methylamino)-4,8-dihydroxy-9,10-anthracenedione

Molecular Formula:  $C_{16}H_{14}N_2O_4$

Molecular Weight: 298.30

Aqueous solubility:  $10^{-9}$  mol/L at 25°C<sup>a</sup>

Log  $K_{ow}$  = 1.61<sup>a</sup>

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<sup>a</sup>Ref. 6.

Table 3. Extinction coefficients of Disperse Blue 26.\*

$\lambda$ , nm	$\epsilon$ , L mol <sup>-1</sup> cm <sup>-1</sup>		
	pH 2.0	pH 7.0	pH 10.8
900	3.17E02	4.05E02	3.26E02
890	3.17E02	4.05E02	3.14E02
880	3.30E02	4.05E02	3.10E02
870	3.36E02	4.21E02	3.14E02
860	3.49E02	4.36E02	3.18E02
850	3.62E02	4.59E02	3.34E02
840	3.74E02	4.74E02	3.53E02
830	3.94E02	4.97E02	3.69E02
820	4.13E02	5.28E02	4.00E02
810	4.38E02	5.51E02	4.20E02
800	4.57E02	5.89E02	4.44E02
790	4.89E02	6.27E02	4.75E02
780	5.20E02	6.66E02	5.10E02
770	5.59E02	7.11E02	5.50E02
760	5.97E02	7.73E02	5.93E02
750	6.47E02	8.26E02	6.44E02
740	6.98E02	8.95E02	7.03E02
730	7.49E02	9.79E02	7.65E02
720	8.19E02	1.06E03	8.40E02
710	8.82E02	1.16E03	9.15E02
700	9.58E02	1.25E03	9.93E02
690	1.03E03	1.35E03	1.08E03
680	1.10E03	1.46E03	1.16E03
670	1.17E03	1.56E03	1.23E03
660	1.25E03	1.66E03	1.31E03
650	1.34E03	1.76E03	1.41E03
640	1.44E03	1.88E03	1.51E03
630	1.54E03	2.01E03	1.62E03
620	1.64E03	2.14E03	1.72E03
610	1.73E03	2.25E03	1.81E03
600	1.80E03	2.32E03	1.88E03
590	1.85E03	2.36E03	1.92E03
580	1.85E03	2.36E03	1.92E03
570	1.83E03	2.31E03	1.88E03
560	1.75E03	2.22E03	1.81E03
550	1.63E03	2.07E03	1.68E03
540	1.48E03	1.86E03	1.51E03
530	1.29E03	1.62E03	1.32E03
520	1.11E03	1.40E03	1.13E03
510	9.52E02	1.19E03	9.54E02
500	8.00E02	1.03E03	7.97E02

Table 3. (cont'd)

$\lambda$ , nm	$\epsilon$ , L mol <sup>-1</sup> cm <sup>-1</sup>		
	pH 2.0	pH 7.0	pH 10.8
490	6.92E02	8.95E02	6.87E02
480	6.16E02	7.96E02	6.04E02
470	5.65E02	7.34E02	5.57E02
460	5.39E02	7.04E02	5.38E02
450	5.39E02	6.96E02	5.30E02
440	5.39E02	7.11E02	5.38E02
430	5.71E02	7.34E02	5.61E02
420	5.97E02	7.73E02	5.97E02
410	6.47E02	8.26E02	6.40E02
400	6.98E02	8.95E02	6.95E02
390	7.81E02	9.79E02	7.65E02
380	8.57E02	1.07E03	8.40E02
370	9.46E02	1.19E03	9.30E02
360	1.04E03	1.32E03	1.03E03
350	1.17E03	1.48E03	1.17E03
340	1.40E03	1.77E03	1.41E03
330	2.07E03	2.62E03	2.03E03
320	2.52E03	3.15E03	2.45E03
310	3.17E03	3.98E03	3.30E03
300	3.94E03	5.12E03	4.29E03
290	4.63E03	5.97E03	4.95E03
280	4.76E03	6.42E03	5.18E03
270	4.57E03	6.58E03	5.79E03
260	4.83E03	6.96E03	5.75E03
250	7.49E03	9.71E03	8.20E03
240	1.62E04	2.04E04	1.65E04
230	2.43E04	3.04E04	2.34E04
220	2.26E04	2.88E04	1.30E04
210	1.77E04	2.33E04	5.93E03
200	9.59E03	2.03E04	5.18E03
190	6.67E03	1.43E04	4.85E03

\*Spectra were recorded in pH 2.0 glycine hydrochloride-glycine, pH 7.0 potassium dihydrogen phosphate-disodium hydrogen phosphate, and pH 10.8 glycine-sodium glycinate. The ionic strength of all buffers was 0.05 M. The wavelength maximum in the visible region (and extinction coefficient) was 581 nm ( $1.85 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup>) at pH 2.0, 584 nm ( $2.36 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup>) at pH 7.0, and 584 nm ( $1.93 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup>) at pH 10.8.

Table 4. Kinetics of the degradation of Disperse Blue 26 in the photoreactor at 300 nm.\*

Water	Initial dye concentration mg/L	Photolysis rate constant, $k_p$ $d^{-1}$	Half-Life d	Quantum Yield $\phi \times 10^5$ mol x Einstein <sup>-1</sup>
organic-free	8	0.1	6.9	4.1
organic-free	5	0.1	6.9	4.1
Hamilton Harbour	5	0.3	2.3	12.4
Grand River	5	0.3	2.3	12.4
Yamaska River	5	0.5	1.4	17.6

\*temperature =  $36 \pm 2^\circ C$ ;  $t_{1/2} = (\ln 2)/k_p$  for first-order reaction

Table 5. Kinetics of the degradation of Disperse Blue 26 in sunlight.\*

Water	Photolysis rate constant, langley <sup>-1</sup>	Half-life, langley	Half-life, d
organic-free	$1.1 \times 10^{-4}$	$6.3 \times 10^3$	10.9
Grand River	$2.2 \times 10^{-4}$	$3.2 \times 10^3$	5.6
Yamaska River	$3.4 \times 10^{-4}$	$2.0 \times 10^3$	3.5
Hamilton Harbour	$4.0 \times 10^{-4}$	$1.7 \times 10^3$	3.0

\*Initial dye concentration 1.0 mg/L; photolyses carried out July 1-11, 1988; noon-time temperature 38°C;  $t_{1/2} = (\ln 2)/k_p$  for first-order reaction.

Table 6. Photolysis of Disperse Blue 26 in the presence of humic acid.\*

Light	[Humic acid], mg/L	Photolysis rate constant, d <sup>-1</sup>	Half-Life, d
summer sunlight	0	6.9	10.0
	5	9.4	7.4
	20	11.1	6.2
	40	10.1	6.8
300 nm	0	14.4	4.8
	5	16.1	4.3
	20	15.7	4.4
	40	17.7	3.9

\*Initial dye concentration 1.0 mg/L and 5.0 mg/L in sunlight and in 300 nm light, respectively.



## FIGURES

Figure 1. Structure of Disperse Blue 26.

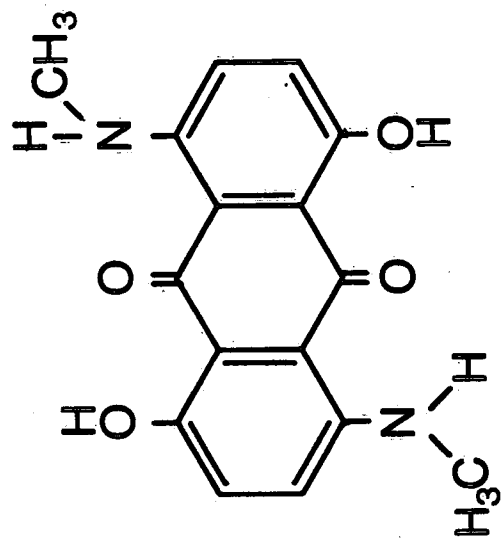
Figure 2. Ultraviolet-visible spectrum of (nominal) 1 mg/L Disperse Blue 26 in water.

Figure 3. High performance liquid chromatogram of technical grade Disperse Blue 26, with absorbance at 220 nm.

Figure 4. Kinetics of disappearance of Disperse Blue 26 in the photoreactor in organic-free water and natural water.

Figure 5. Kinetics of disappearance of Disperse Blue 26 in sunlight in organic-free water and natural water.

Figure 1



DISPERSE BLUE 26

Figure 2

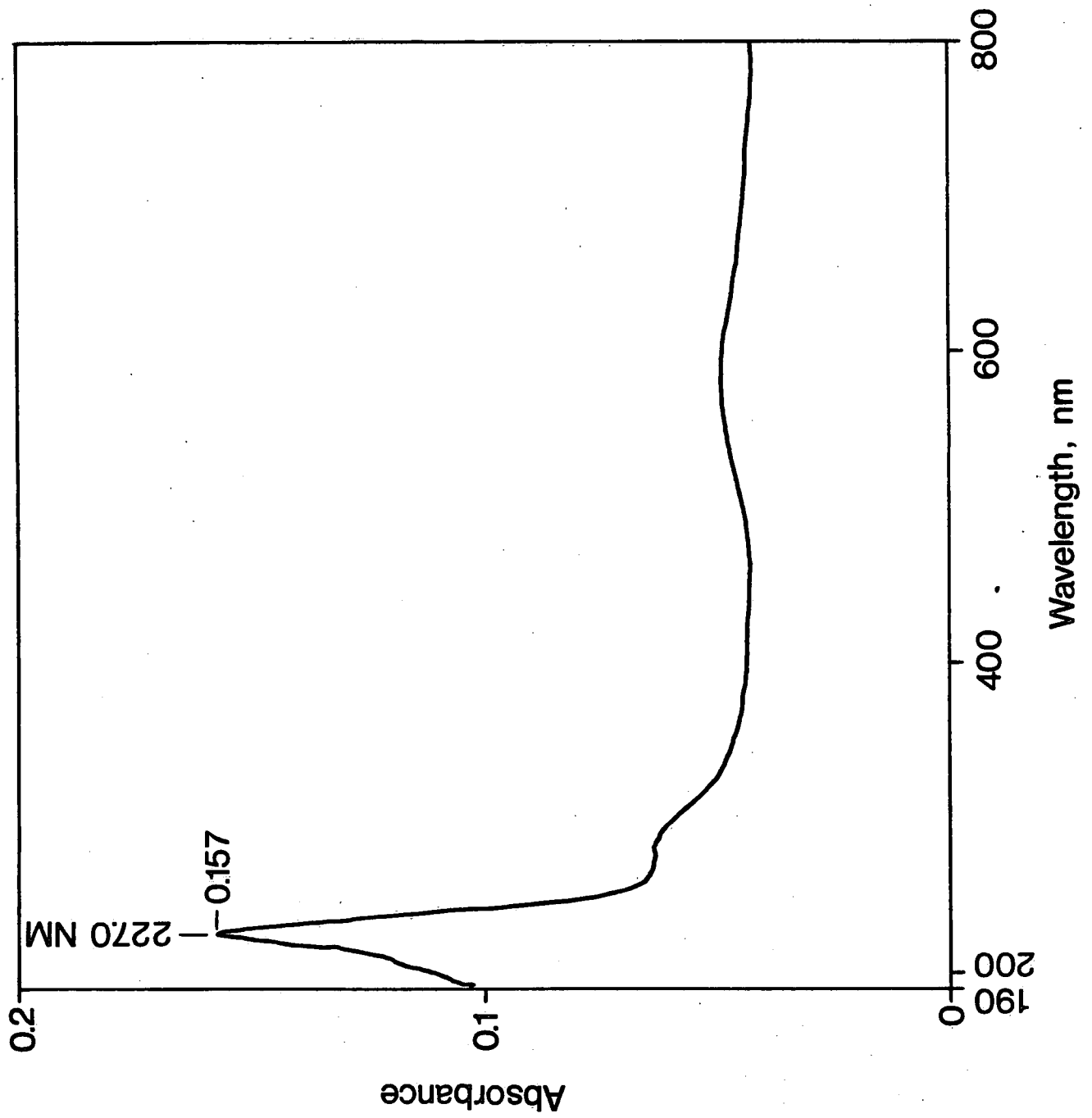


Figure 3

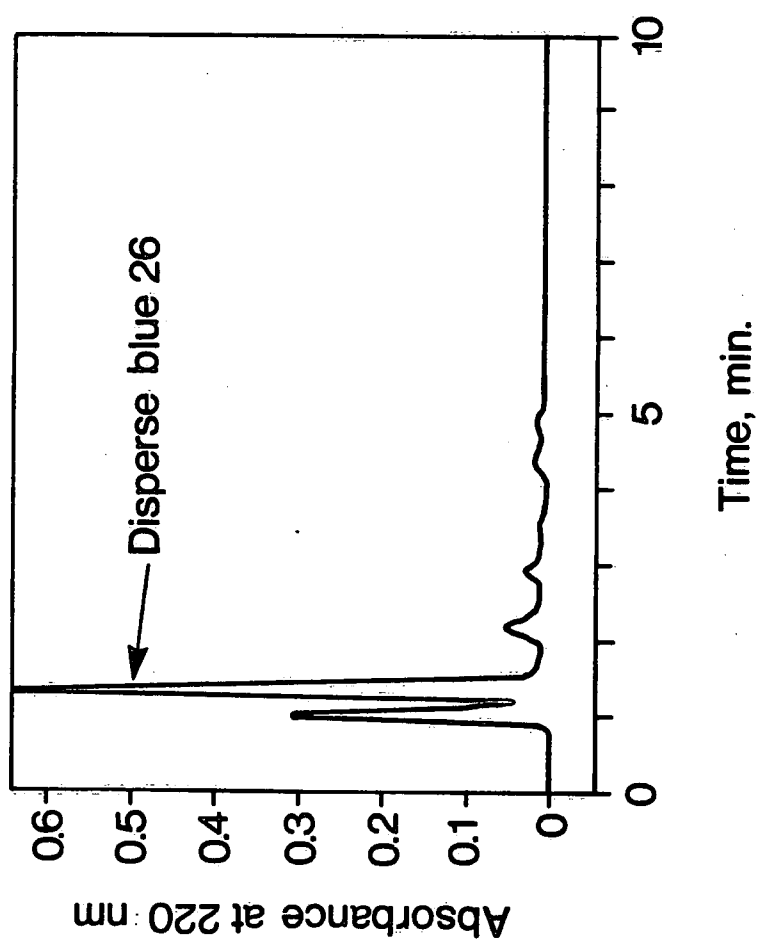


Figure 4

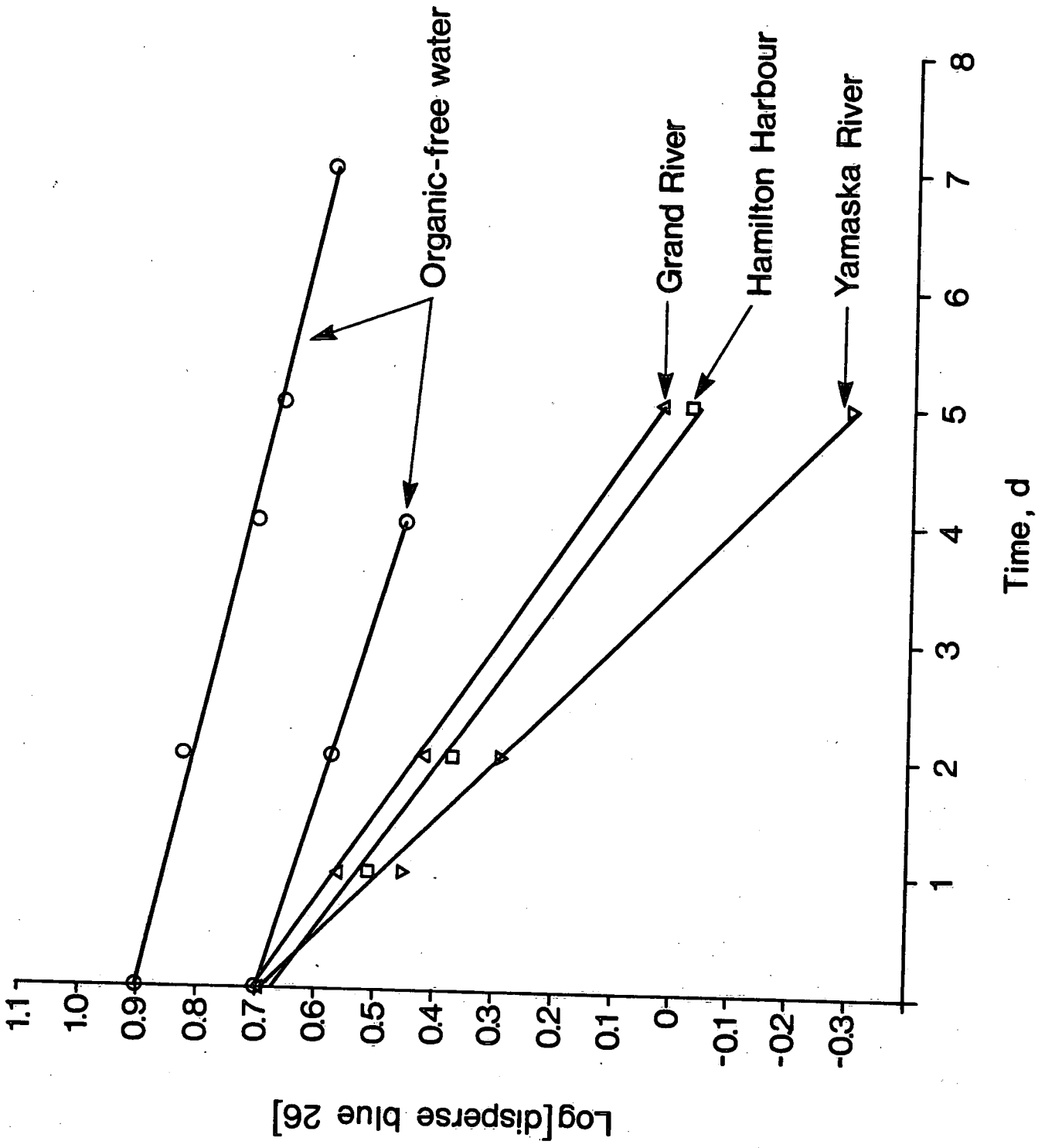


Figure 5

