

# Light Absorption by Yellow Substance in Storm Runoff from Log Handling Areas at a Timber Export Port, Tauranga, New Zealand

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## ABSTRACT

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Spectral values of light absorption by yellow substance at near ultraviolet to visible wavelengths were measured in 22 storm runoff samples from the wharf log handling areas at the Port of Tauranga, New Zealand, to ascertain the feasibility of measuring light absorption for monitoring yellow substance in storm runoff. As in previous research on natural marine and inland waters, the spectral shapes of yellow substance absorption in storm runoff from the wharf log handling areas fitted an exponential model. The spectral slope varied only slightly, though the suspended solid concentration of the samples varies from 9.2 to 1,100 mg/l. The overall mean  $g_{440}$  was  $17.9 \text{ m}^{-1}$ , 85 and 160-1,280 times that of natural marine waters in the Tauranga Harbour and around the South Island of New Zealand. The method appears feasible for rapid monitoring of yellow substance in storm runoff from log handling areas and provides a basis for tracing dispersion of the storm effluent in the receiving tidal waters.

**ADDITIONAL INDEX WORDS:** Aquatic humus, pollution, dissolved organic carbon.

## INTRODUCTION

Yellow substance, the filter-passing organics (dissolved and colloidal), known as "aquatic humus" (THURMAN, 1985), is responsible for absorbing most of the light from the sun entering waters and imparting a yellow colour to waters by selective absorption of blue light. It was initially called "Gelbstoff" by KALLE (1938, cited by BRICAUD *et al.*, 1981), *i.e.*, yellow substance, and more recently "gilvin" (KIRK, 1976).

Yellow substance, present in nearly all natural waters in different quantities, is typically the largest single category of components of the dissolved organic carbon (DOC), and there is an overall correlation of DOC and light absorption (GRIEVE, 1985). As light absorption by yellow substance amounts to direct competition with phytoplankton for capture of photosynthetically available radiation from the sun and also changes the colour of natural waters by shifting the energy of maximum transmission to longer wavelengths, investigations of light absorption by yellow substance in lake, river and marine waters have been carried out (KIRK, 1976; BRICAUD *et al.*, 1981; DA-

VIES-COLLEY and VANT, 1987; and DAVIES-COLLEY, 1992).

Absorption spectra for filtered water samples usually follow an exponential pattern over much of the ultraviolet (UV) to visible spectrum (KIRK, 1976). This exponential absorption spectrum was represented by BRICAUD *et al.* (1981) by the following expression:

$$g_{\lambda} = g_R \exp[S(R - \lambda)] \quad (1)$$

Where:

$g$  = the absorption coefficient ( $\text{m}^{-1}$ )

$\lambda$  = wavelength (nm)

$R$  = a reference wavelength (nm)

$S$  = a parameter characterising the slope of the exponential curve

Previous researchers (KIRK, 1976; BRICAUD *et al.*, 1981; DAVIES-COLLEY and VANT, 1987; DAVIES-COLLEY, 1992) have indicated that the exponential model was a satisfactory representation of the absorption spectra of yellow substance in a wide variety of waters.

To date, no comparative study of light absorption by yellow substance appears to have been carried out on storm runoff. This is particularly



Figure 1. The Port of Tauranga and Tauranga Harbour.

true of storm runoff from wharf log handling areas in which concentrations of yellow substance may be appreciably higher than in the river, lake and marine waters away from leaching of bark. The aims of this paper are:

- (1) to investigate whether Equation 1 is a useful model of light absorption by yellow substance in storm runoff from log handling areas; and
- (2) to test whether light absorption coefficients of water samples at certain wavelengths (for example, at 440 nm) may represent the concentration of yellow substance, and thus provide a basis for estimating extent of mixing of "coloured" storm runoff from log handling areas in receiving waters.

This investigation relates specially to the new Sulphur Point wharf development at the Port of Tauranga, New Zealand (Figure 1), which was constructed in 1991–1992.

#### METHODS

Eight sampling sites were chosen around the Sulphur Point wharf to investigate the storm run-

off quality. Figure 2 shows the details of sampling sites. The samples were collected in 1 litre polypropylene bottles and stored chilled in the dark immediately after sampling. In the laboratory, the determination of light absorption by yellow substance in the storm runoff samples was carried out within 48 hours.

The samples were filtered with precombusted (15 minutes at 550 °C) Whatman GF/C glassfibre filters before undertaking analysis with a double-beam Hitachi 150-20 spectrophotometer. Filtered samples contained in a 10 mm path length cuvette were scanned at 200 nm/min from 200 to 750 nm. In all work, matched cuvettes were employed and the reference cuvette contained distilled water. The apparent absorption coefficient,  $\chi_\lambda$  (natural log base) was calculated from the absorbance,  $D_\lambda$ , as

$$\chi_\lambda = 2.303 D_\lambda / r \quad (2)$$

where  $\lambda$  is wavelength (nm) and  $r$  is cuvette path length (10 mm).

Even after filtration, the filtrate still remains a scattering medium because small particles pass

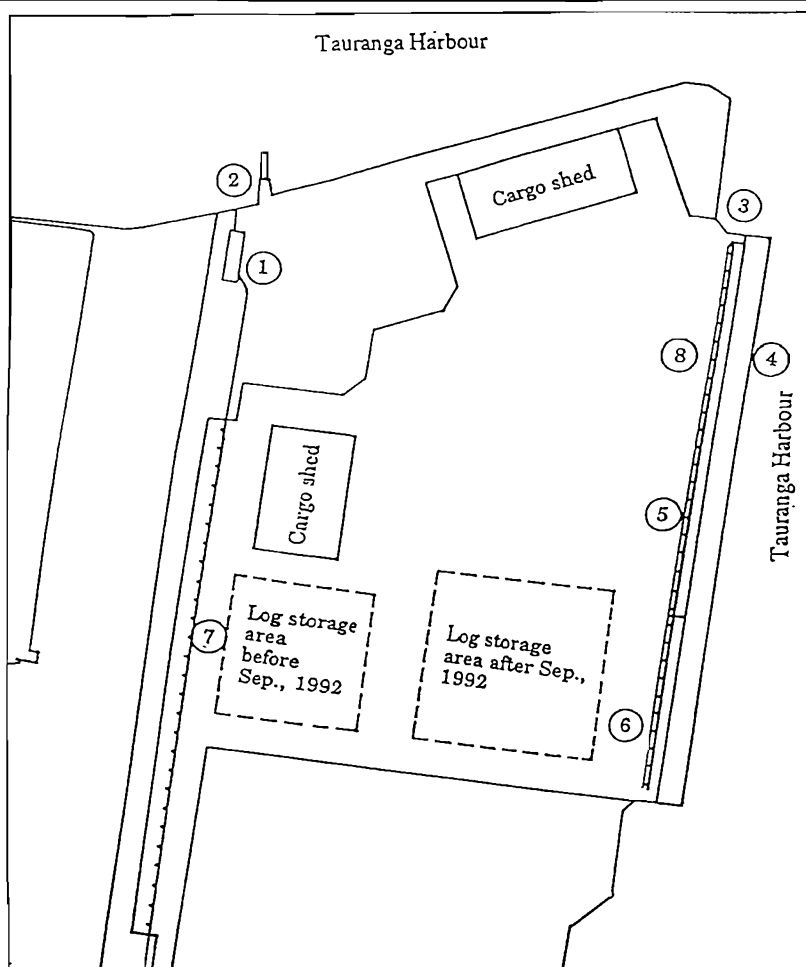


Figure 2. Sampling sites at the Sulphur Point wharf.

through the filter. Therefore, the actually measured absorbance by conventional spectrophotometer (without a diffuse reflectance accessory) is intermediate between the attenuation coefficient and absorption coefficient. Based on the two assumptions that true absorption is negligible at long wavelength ( $L$ ) and that the residual scattering is inversely proportional to wavelength ( $\lambda$ ) (BRICAUD *et al.* 1981), the true absorption coefficient can be calculated with the following equation:

$$g_{\lambda} = \chi_{\lambda} - \chi(L)(L/\lambda) \quad (3)$$

The research by BRICAUD *et al.* (1981), DAVIES-COLLEY and VANT (1987) and DAVIES-COLLEY (1992) confirms the method.

In this study, the true absorption coefficient is calculated with Equation 3 taken as 740 nm for comparison with previous research.

A total of 22 samples was examined. Twenty were taken from the log handling areas or the areas affected by the log handling (sites 1-7). Two were taken from areas unaffected by the log handling at time of sampling (site 8).

## RESULTS

After correction with Equation 3, absorption coefficient vs. wavelength were plotted on a semi-log scale (Figures 3 and 4). As the apparent absorption spectra do not vary regularly when wavelengths are less than 300 nm, only those absorption values from 300 to 700 nm were plotted.

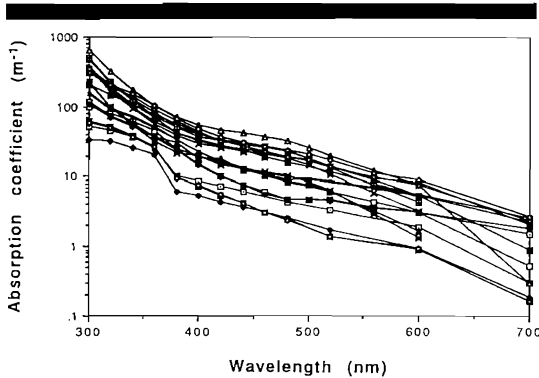


Figure 3. Absorption spectra of the 20 samples from the log handling areas at Sulphur Point wharf.

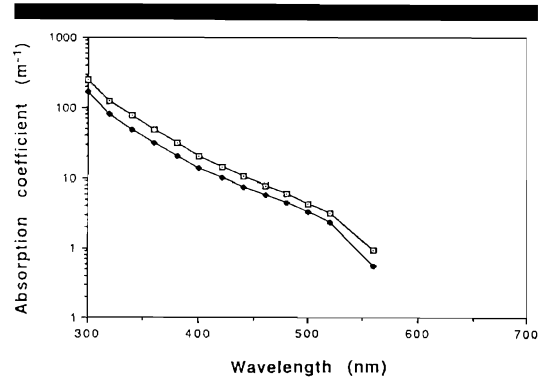


Figure 4. Absorption spectra of the 2 samples from the wharf area which were not affected by log handling at Sulphur Point wharf.

From Figures 3 and 4, it is evident that all the absorption spectra of 22 samples, of which the suspended solid concentration and turbidity vary from 9.2 to 1,100 mg/l and 0.9 to 450 NTU, are close to straight lines. Curve fitting results show that all correlation coefficients for the 20 samples from the log handling areas are more than 0.87. The overall mean correlation coefficient is 0.93. For the two samples from the wharf surface not affected by log handling, the average correlation coefficient is 0.98.

The curve fitting results indicate that the slope  $S$  of the 20 samples from the log handling areas does not vary greatly. The absorption coefficients of these samples vary appreciably ( $g_{440}$  ranged from 3.5 to 41  $m^{-1}$ , with a mean value of 17.9  $m^{-1}$ ;  $g_{340}$  from 26 to 180  $m^{-1}$ , with a mean value of 85.6  $m^{-1}$ ). The overall mean  $S$  value of the 20 storm runoff samples from the log handling areas was found to vary from 0.010 to 0.016  $nm^{-1}$  with a mean value 0.0127  $nm^{-1}$  ( $SD = 0.0016 nm^{-1}$ ). This suggests that the spectral pattern of absorption does not vary greatly in spite of a wide range of SS and VSS concentrations. The  $S$  values of the two samples from the wharf area without log handling effects are respectively 0.019  $nm^{-1}$  and 0.017  $nm^{-1}$ . The mean value, 0.018  $nm^{-1}$ , is higher than that of the samples from the log handling areas. Mean  $g_{440}$  and  $g_{340}$  values for these two samples are respectively 8.9  $m^{-1}$  and 62.1  $m^{-1}$ .

## DISCUSSION

### Concentration of Yellow Substance

Absorption coefficients at wavelengths 340 nm, 375 nm, 400 nm, 420 nm, and 440 nm were used

as an index of yellow substance concentrations by previous researchers (BURT, 1958; KALLE, 1961, cited by BRICAUD *et al.*, 1981; KIRK, 1976; BRICAUD *et al.*, 1981; DAVIES-COLLEY and VANT, 1987).  $g_{440}$  relates to absorption in the visible region of the spectrum and is of more interest than the UV from the perspective of aquatic plant production or the aesthetics of water bodies. Therefore,  $g_{440}$  is more often used in recent studies as an index of yellow substance concentration. In this study,  $g_{440}$  is used as an index of concentration of yellow substance. Comparatively, the arithmetic mean value of  $g_{440}$  for the 20 samples from the log handling area, 17.9  $m^{-1}$ , is considerably higher than that of the natural marine and inland waters tested in previous research and in this study.

KIRK (1976) reported that the  $g_{440}$  values ranged from 0.97  $m^{-1}$  to 6.7  $m^{-1}$  in several inland freshwater bodies in New South Wales, Australia. DAVIES-COLLEY and VANT (1987) reported that the  $g_{440}$  values for 12 New Zealand lake waters ranged from 0.09 to 4.87  $m^{-1}$ . Only in some remarkably highly coloured freshwaters, such as some humic bog and bog lake waters and the highly coloured tropical rivers, are the yellow substance concentrations as high as in this case. For example, the concentrations of yellow substance are respectively 19  $m^{-1}$  and 12.4  $m^{-1}$  for two very high coloured natural waters in Lough Napeast, Ireland (JEWSON and TAYLOR, 1978) and in the Carrao River, Venezuela (LEWIS and CANFIELD, 1977, cited by KIRK, 1983). Evidently the storm runoff from the log handling areas is comparable to "bog water". Comparing inland waters, the yellow substance concentrations in ocean and coastal waters

are lower. KIRK (1983) summarized the concentrations of yellow substance in different marine waters. The  $g_{440}$  values of samples from different oceanic waters, including Atlantic, Pacific and Indian Oceans, range from nearly zero to  $0.16 \text{ m}^{-1}$ . The concentration of yellow substance in coastal and estuarine waters, often affected by discharges from land, ranges from  $0.02$  to  $1.89 \text{ m}^{-1}$ , higher than that of oceanic waters. DAVIES-COLLEY (1992) reported that  $g_{440}$  in natural marine waters around the South Island, New Zealand, ranges from  $0.014$  to  $0.11 \text{ m}^{-1}$ . In humic-stained surface water in Doubtful Sound (coastal area), New Zealand, the concentration of yellow substance is  $1.8 \text{ m}^{-1}$ . In this study the  $g_{440}$  values of the 35 natural water samples from the Tauranga Harbour taken at different depths and different tide conditions ranged from  $0.12$  to  $0.40 \text{ m}^{-1}$ , with a mean value of  $0.21 \text{ m}^{-1}$  which is much lower than the storm runoff samples from the wharf surface.

However, the concentration of yellow substance in the two samples from the wharf area not affected by the log handling,  $8.9 \text{ m}^{-1}$ , was not considerably lower than that of the samples from the log handling areas, though the sampling surface looked clear when sampled. This is probably because runoff from this area was polluted by other cargoes and surface dirt which did not appear obvious to the naked eye.

#### Mean Spectrum Slope $S$

The overall mean spectrum slope of the 20 samples from the log handling areas,  $0.0127 \text{ nm}^{-1}$  ( $SD = 0.0016 \text{ nm}^{-1}$ ), is lower than that reported by previous researchers on natural inland waters but consistent with natural marine waters. The mean spectrum slope of the two samples from the wharf surface not affected by log handling,  $0.018 \text{ m}^{-1}$ , is higher than that of marine waters but consistent with that of inland waters. DAVIES-COLLEY and VANT (1987) indicated that the mean slope  $S$  for 11 New Zealand lakes is  $0.0187 \text{ nm}^{-1}$  ( $SD = 0.0016 \text{ nm}^{-1}$ ). The mean slope  $S$  for 22 Australian inland waters obtained by KIRK (1976, cited by DAVIES-COLLEY and VANT, 1987) is  $0.0161 \text{ nm}^{-1}$  ( $SD = 0.0016 \text{ nm}^{-1}$ ). BRICAUD *et al.*'s (1981) investigation on 8 various seawaters shows that the average slope  $S$  of the spectra is  $0.014 \text{ nm}^{-1}$  ( $SD = 0.0032 \text{ nm}^{-1}$ ). Generally less steep absorption spectra have been reported for humic extracts, (e.g., KALLE, 1966 reported spectra for which  $S = 0.008 \text{ nm}^{-1}$ , cited by DAVIES-COLLEY and VANT, 1987). Accordingly, it is probable that storm run-

off polluted by bark has a lower mean  $S$  value because it contains more humic material and the unpolluted storm runoff has a higher mean  $S$  value because it contains less humic matter.

#### CONCLUSIONS

The shapes of the absorption spectra by yellow substance in storm runoff samples from log handling areas, suitably corrected for residual light scattering in the spectrophotometer, can be well described by the following exponential function of wavelength,  $\lambda$ , at near UV through to visible wavelengths (300–700 nm):

$$g_{\lambda} = g_{R} \exp[0.0127(R - \lambda)]$$

This result is in accord with other researchers' results on a variety of natural marine and inland waters (KIRK, 1976; BRICAUD *et al.*, 1981; DAVIES-COLLEY and VANT, 1987; DAVIES-COLLEY, 1992), and demonstrates that it is feasible to develop a rapid method for monitoring yellow substance in storm runoff from log handling areas of ports by absorption measurements. The method provides a basis for tracing dispersion of the storm effluent in the receiving tidal waters.

The overall mean concentration of yellow substance (taking  $g_{440}$  as an index) in storm runoff from the log handling area is  $17.9 \text{ m}^{-1}$  which is some 85 and 160–1,280 times that of natural marine waters in the Tauranga Harbour and around the South Island, New Zealand. As the concentration of yellow substance in storm runoff from the log storage areas is high, there will not be a large error for measuring  $g_{440}$  directly as an index of yellow substance concentration.

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