

Seasonal influence on the DOC-UV relationship in water

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Abstract

A relationship between the concentration of dissolved organic carbon (DOC) and the absorption of ultraviolet light (UV) can in principle be utilized to substitute DOC measurements by the more rapid and simpler UV measurements. Although many factors are known to influence the DOC-UV absorption relationship in water, the effect of seasonal variation has seldom, if ever, been mentioned. Collected data over a period of two years indicated the effect of seasonal changes and it was found that temperature of the water source was responsible for a fluctuation of 16% in the DOC-UV relationship.

Introduction

Virtually all surface waters are recipients of wastes such as treated wastewater, agricultural runoff and industrial effluent, however, most treatment processes are not effective in removing many organic pollutants. Furthermore, certain organic compounds have been shown to be precursors for the formation of undesirable by-products such as organic chloro-compounds when potable water supplies are disinfected with chlorine, and this has resulted in large-scale investigations on the removal of these precursors. (Jolley, 1975-1981).

Organic micropollutants (the microgram or less per litre level) are usually determined by means of gas chromatography/mass spectroscopy (Keith, 1981). Overall organic macropollution (mg/l level) can be determined with an organic carbon and/or organohalogen analyser (Van Steenderen, 1981). These sophisticated analytical instruments are not within the reach of most water purification works, and it is therefore essential to develop valid, though less complicated and less costly analytical techniques for organic compounds which can be used on a routine basis.

Many organic compounds commonly found in surface waters absorb ultraviolet radiation, which has motivated researchers to establish a relationship between ultraviolet absorption (UV) measurements and the concentration of dissolved organic carbon (DOC) (Bremer *et al.*, 1966). Although modern organic carbon analysers enable accurate determination of the DOC content normally encountered in potable water, the initial outlay for this instrumentation is relatively high when compared with that for a single-beam UV spectrophotometer.

Various practical applications of a DOC-UV relationship have been reported for the evaluation of water and wastewater (Dobbs *et al.*, 1972), drinking-water (Bremer *et al.*, 1966), the characterization of pulp and paper bleach effluent (McLachlan, 1981) and active carbon exhaustion (Van Steenderen, 1984). Although it is generally accepted that such relationships are not unique, the poor association often found between DOC and UV measurements for water of relatively constant chemical quality has led to some doubt as to their validity.

Fluctuations in the DOC-UV relationship of a specific type of water can be attributed to fluctuations of turbidity, inorganic UV-absorbing compounds, organic compounds which do not ab-

sorb UV light, and chromophores. The first two potential sources of error can largely be overcome by optimizing experimental conditions i.e. filtration of the sample and measuring UV absorption at a wavelength where nitrates do not absorb. The fluctuations are due to the organic composition of the water and could be the reason that the ratio of UV-absorbing material to non-UV-absorbing material is often variable.

In this paper the influence of temperature on the DOC-UV relationship in Rand Water Board (RWB) water as supplied to the Pretoria Municipal area is investigated. This follows an earlier report concerning the occurrence of trihalomethane compounds in these same waters (Van Steenderen *et al.*, 1983).

During the first year of the survey, monthly grab samples were collected from six service reservoirs and their corresponding distribution network (a total of 12 samples per month) to determine whether there was any useful relationship between DOC and UV in practice. The second year saw more intensive sampling of only one of these 12 points to determine factors specifically responsible for the fluctuation in this relationship.

Experimental procedures

Samples were collected in glass containers and analysed immediately upon arrival at the laboratory. Ultraviolet absorption for this water gave the best response when measured at 275 nm using a 40 mm quartz cell. DOC was measured according to the procedures described by van Steenderen and Lin (1981). Water temperature data from the river draw-off point were supplied by the Rand Water Board.

Results and Discussion

Using pooled results (of the first year), whereby DOC was regressed on UV, yielded a correlation coefficient of 0,75 based on a 95% level of significance. Analysis of individual sampling points gave similar results. However, a time-series plot typically yielded a roughly bi-modal pattern (Fig. 1); two maxima, with DOC and UV out of phase at the first but in phase at the second, were exhibited. This suggests that the degree of association between DOC and UV depends on the time of the year the samples were taken. Linear regression of DOC upon UV, but using seasonal data, gave better correlation coefficients:

Winter	$r = 0,91$	— based on 17 samples per season
Spring	$r = 0,86$	
Summer	$r = 0,92$	
Autumn	$r = 0,98$	

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A general linear relationship between DOC and UV may be presented by -

$$\text{DOC} = c + m(\text{UV})$$

Where: c = the amount of DOC due to substances not absorbing UV light;

and

m = the average number of carbon atoms per number of chromophores in the organic molecules in the water.

For an out of phase change between DOC and UV, the relationship $\delta(\text{DOC}) = \delta c + \delta m(\text{UV}) + m\delta(\text{UV})$ can be formulated, implying that for -

$$\delta(\text{DOC}) > 0 \text{ and } \delta(\text{UV}) < 0$$

- if $\delta c < 0$ then $\delta m > 0$
- if $\delta m < 0$ then $\delta c > 0$; and for

$$\delta(\text{DOC}) < 0 \text{ and } \delta(\text{UV}) > 0$$

- if $\delta c > 0$ then $\delta m < 0$
- if $\delta m > 0$ then $\delta c < 0$

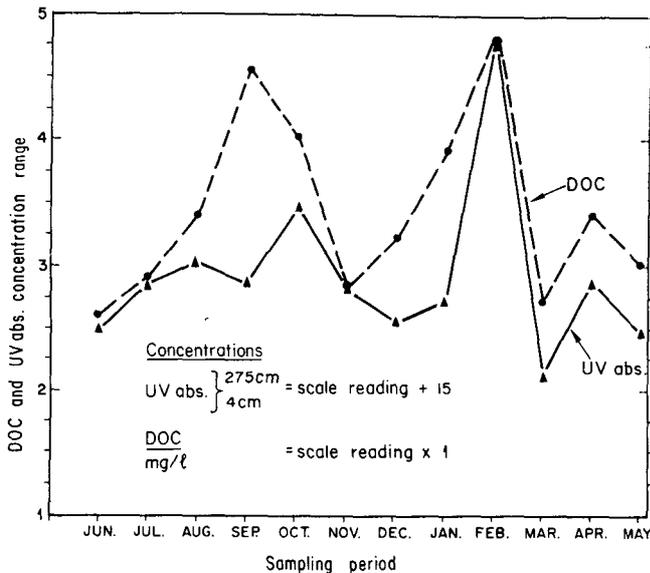


Figure 1
Ultraviolet absorption (UV) and dissolved organic carbon concentration (DOC) profiles for a one-year cycle

This means that when DOC and UV change out of phase, any change in c (or m) is accompanied by an opposite change in m (or c) (Fig. 2). A plot of m against c confirmed this and showed that over the range of observations this change was linear (Fig. 3).

One can, at this stage, only speculate about the reason for the opposite changes in m and c . One possibility is that, during the warmer times of the year, UV light absorbing molecules split off saturated molecules.

The first half of the second year of sampling confirmed what had been found during the previous year. However, during the second half, the seasonal effect on the DOC-UV relationship was not as pronounced as found previously. This could be explained by the considerable changes in water composition during this period (detected by means of electrical conductivity measurements), probably as a result of the mixing of water from different sources in the distribution reservoirs.

Since time of the year clearly influenced the DOC-UV rela-

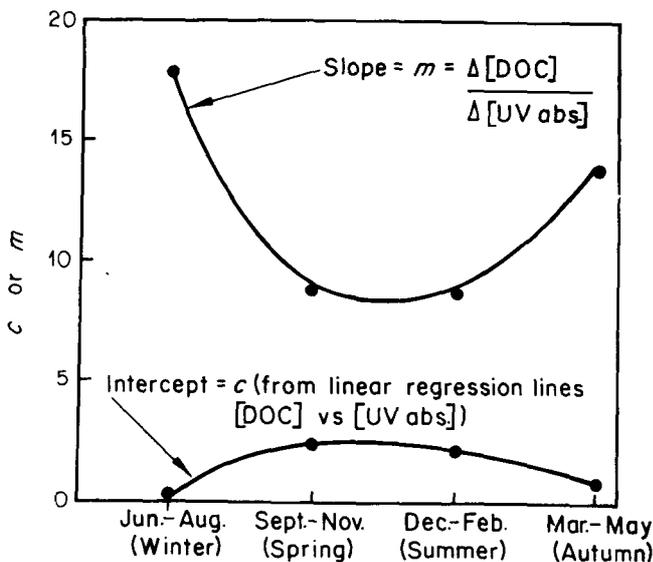


Figure 2
Seasonal effect on the relationship between DOC and UV

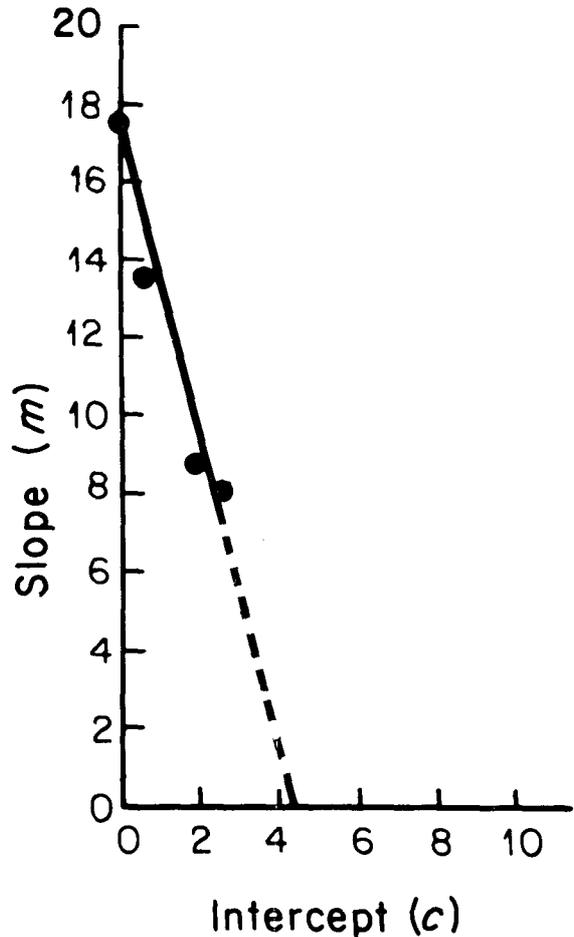


Figure 3
The relationship between the parameters c and m in the relationship $\text{DOC} = c + m(\text{UV})$

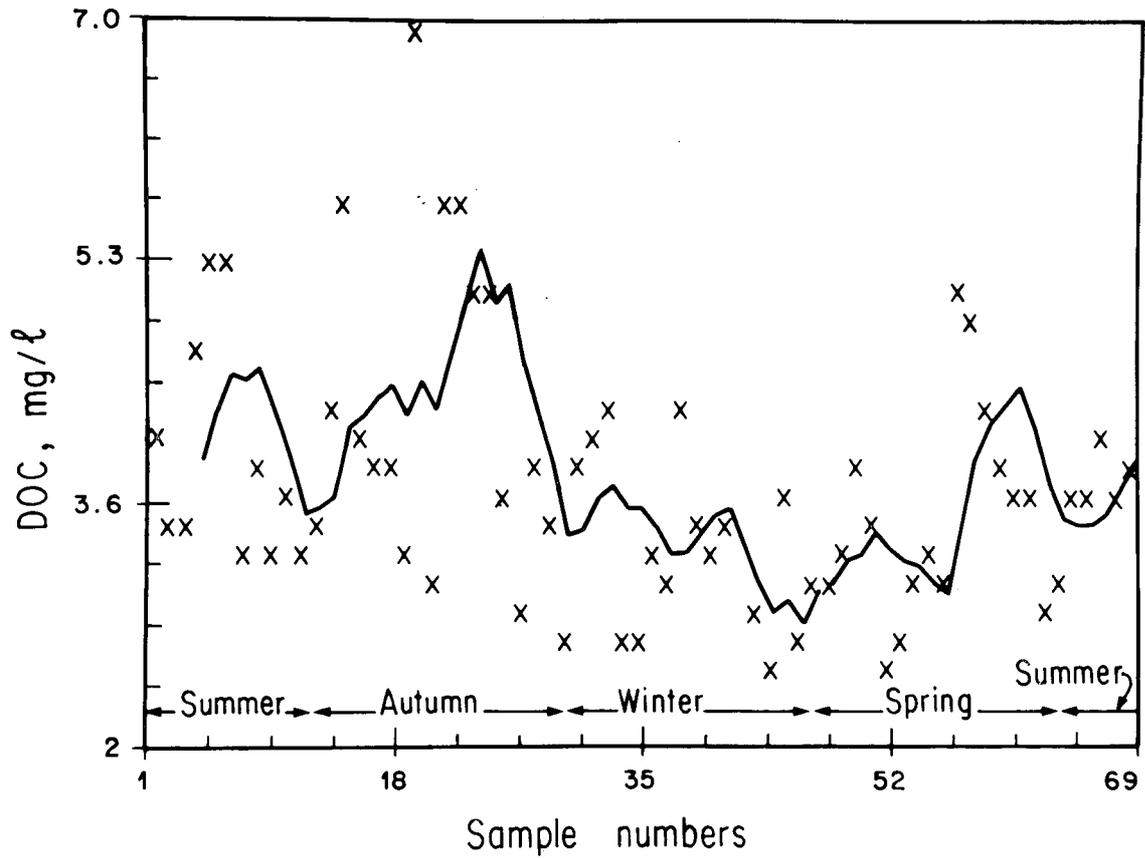


Figure 4
 DOC profile from a single sampling point over a one-year cycle
 (Plotted as a moving average of five points.)

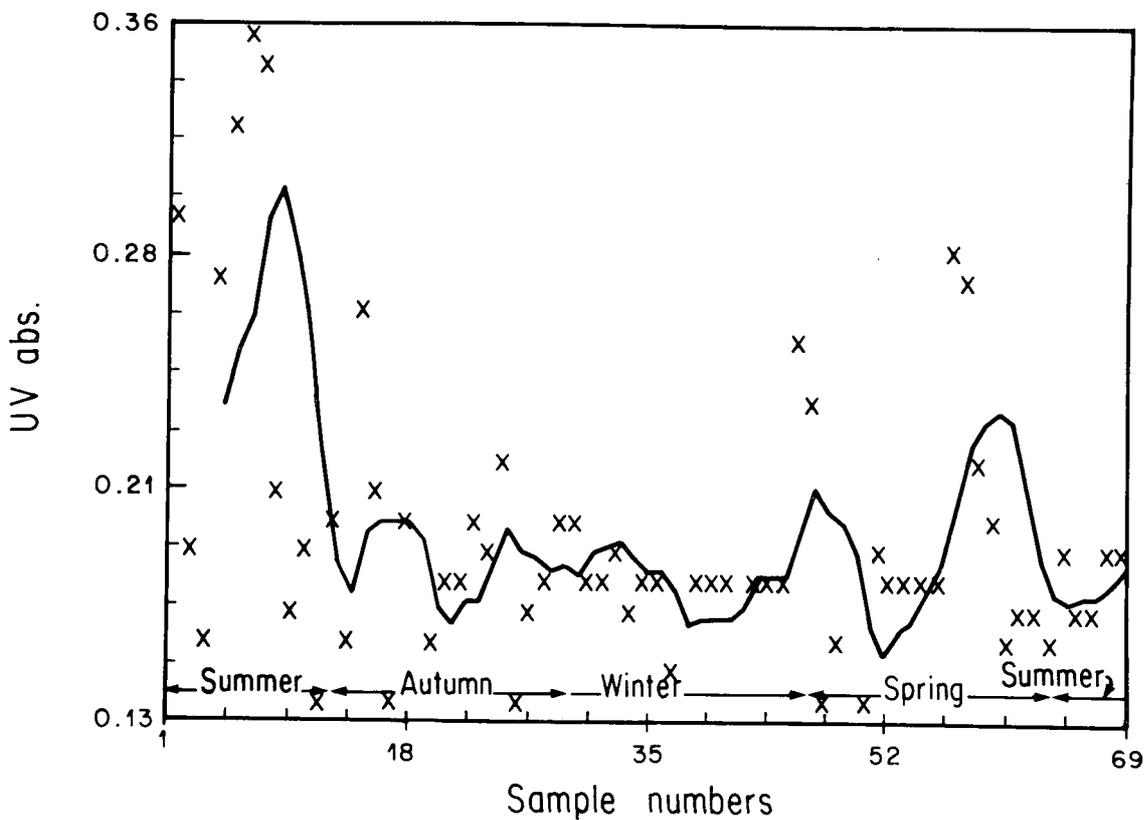


Figure 5
 UV profile from a single sampling point over a one-year cycle
 (Plotted as a moving average of five points.)

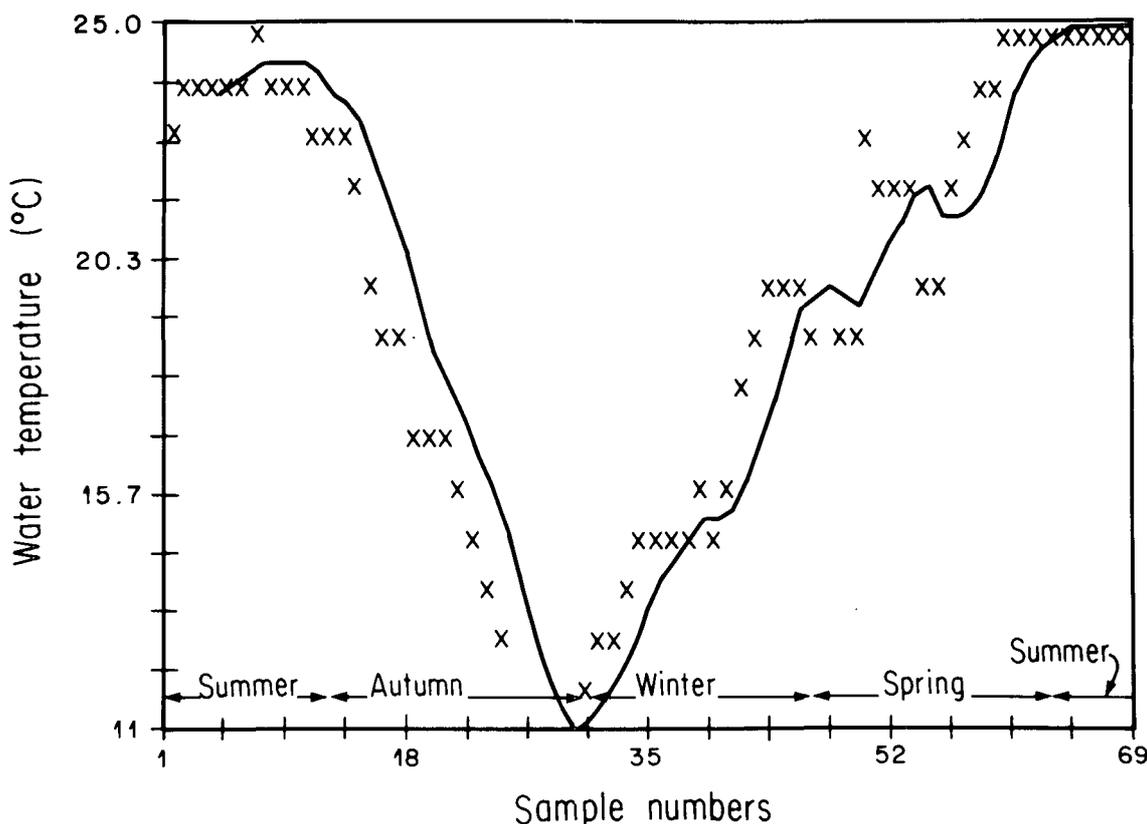


Figure 6
Water temperature profile from a single sampling point over a one-year cycle (Plotted as a moving average of five points.)

relationship, the significance of water temperature was examined more closely. Multiple linear regression analysis between the variables DOC, UV and water temperature (values obtained from Figs 4 to 6 for the period 1981 – 1982) indicated that 16% of the variation in UV readings during this sampling period was attributable to a fluctuation in water temperature at the raw water intake. This temperature effect was found to be irreversible once the water had reached its destination in the city.

Based on a 99% confidence level, the DOC-UV relationship was found to be $DOC = 2,58 + 6,63 UV$ with a coefficient of variability of 22%. No correlation was found between DOC and water temperature.

Conclusion

The advantages of obtaining a practical relationship between DOC and UV for a particular water are of great benefit since UV measurements are easily carried out, rapid and relatively inexpensive when compared with DOC instrumentation. However, this relationship must be approached with caution since a two year survey indicated that it can probably be influenced by seasonal factors as well.

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