Measurement of Light Environment with a Chemical Radiation Meter Using Anthracene-Ethyl Alcohol Solution

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Abstract
The anthracene method which is one of the techniques for assessing the light environment in ecological studies, is described with a view to utilizing it for practical applications. This method is based on the photochemical reaction of anthracene in an alcohol solution. The advantages of the method are that the light environment can be measured in many positions at the same time regardless of the weather conditions. The disadvantages are that the method tends to be time-consuming for the derivation of basic regression equations and the procedures preceding and following the field measurements, and that the chemical reaction is related to ultraviolet radiation, although the regression is usually derived based on the calculation of the photon flux density, illuminance or total irradiance. These characteristics are described along with the theory of the method. Practical procedures for laboratory and field measurements are described with some examples on the estimation of relative radiation in forests.

Discipline: Forestry and forest products
Additional key words: anthracene method, relative radiation

Introduction
Light measurement is important for the analysis of the structure and function of forests and other plant communities. Although photosensors are generally used, measurements of instantaneous light flux values fluctuate considerably in a forest, due to the presence of sunflecks under sunny skies. To alleviate this shortcoming a large number of photosensors could be used simultaneously to compensate for the large variations in the light values. This approach is, however, often unpractical for economic reasons. Therefore in practice, the use of photosensors is limited to cloudy days for the measurement of steady-state relative light flux density. This limitation may lead to the collection of an insufficient number of data when working under a tight schedule. We describe here a simple method using a chemical radiation meter that utilizes anthracene. It has some advantages that cannot be met by the conventional methods of light measurement.
measurement with photosensors.

The chemical radiation meter described here measures the radiation based on the photochemical reaction of anthracene (C₁₄H₁₀), which is soluble in organic solvents such as alcohol or benzene. Upon the exposure to solar radiation (ultraviolet radiation), anthracene in the solution polymerizes into insoluble dianthracene ((C₁₄H₁₀)$_2$). Thus the radiation amount can be calculated by measuring the concentration of anthracene before and after the exposure. This technique is hereafter referred to as the anthracene method.

The anthracene method which was first introduced by Dore[2], was applied to measurements in forests and to the evaluation of herbicide tests[8,9,13]. Benzene was used as a solvent. Thereafter, radiation measurements were performed in forests using an anthracene-ethyl alcohol solution[1,4,6,12] due to the ease of handling. Detailed examinations were carried out to obtain more accurate measurements[3,11]. Here we describe a chemical radiation meter using the anthracene-ethyl alcohol solution proposed by Hagihara et al.[3,4], in relation to applications to forest ecological studies.

**Theory and characteristics of the anthracene method**

1) **Principle of the method**

Anthracene-ethyl alcohol solution shows an absorption spectrum with peaks in the 250-400 nm range. The relationship between the absorbance $D$ and concentration of anthracene $C$ (mg/l) is expressed by the function:

$$D = kC,$$

where $k$ is a coefficient. The values of $k$ at some wavelengths with higher peaks of absorption, using a quartz cell 10 mm wide, are $4.407 \times 10^{-2}$ l/mg at 356.8 nm, $4.219 \times 10^{-2}$ at 375.9 nm and $2.149 \times 10^{-2}$ l/mg at 350 nm[3].

Anthracene in ethyl alcohol polymerizes into insoluble dianthracene upon exposure to solar radiation. The relationship between the concentration of anthracene $C$ and the integrated radiation $I$ is expressed as:

$$C = A \exp(-\mu I), \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ sol
Fig. 1. Relationship between the concentration of anthracene in the solution (C) and
the integrated photon flux density (I).\(^3\)

The experiment was conducted using vials with caps upward.

an integrated parameter. On the other hand, the disadvantages of the method are as follows:
(1) the procedures for the application of the method before and after field work are time­
consuming; (2) the reaction of anthracene is related to ultraviolet radiation and not to the
total radiation or photosynthetically active radiation, although the regressions are obtained
based on PFD, illuminance or total irradiance; (3) the light environment is evaluated only at
the integrated level.

Application of the anthracene method

The procedures for the preparation of the anthracene-ethyl alcohol solution and for the
field measurements are as follows. It must be emphasized that since a large quantity of alco-
hol is used in the whole process, care must be taken to avoid fire. Also anthracene may cause
skin irritation\(^9\).

1) Determination of concentration

The maximum amount of radiation measurable with this method is smaller when the con-
centration of the anthracene solution is higher. Table 1 lists approximate maximum values of
integrated PFD and lower limits of concentration based on Fig. 1. On the other hand, the
value of \(\mu\) is larger when the concentration of the solution is higher, suggesting that the sen-
sitivity is higher when the concentration of the solution is higher. Thus the anthracene con-
centration must be determined based on the amount of solar radiation in the seasons and
the location of the measurement. Table 1 can
Table 1. Approximated figures of the maximum integrated photon flux density measured by using the solution and corresponding concentration of residual anthracene

<table>
<thead>
<tr>
<th>Initial concentration (mg/l)</th>
<th>Maximum integrated PFD (E/m²)</th>
<th>Concentration of residual anthracene (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>160</td>
<td>20</td>
<td>10</td>
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<tr>
<td>80</td>
<td>22</td>
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<tr>
<td>10</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>38</td>
<td>1.5</td>
</tr>
<tr>
<td>2.5</td>
<td>52</td>
<td>0.6</td>
</tr>
</tbody>
</table>

The values were cited from Fig. 1. The experiment was conducted using vials with caps upward.

be used to estimate the approximate concentration of anthracene under various conditions.

The concentration is estimated by measuring the absorbance with a spectrophotometer. Wavelength of the measurement should be determined by considering the appropriate range of measurements of the instrument.

2) Preparation of anthracene-ethyl alcohol solution

Materials and instruments are as follows: anthracene; ethyl alcohol (99%) required for both the solution and other preparation procedures; a bottle (large enough to make the solution); a magnetic stirrer; a balance (precision: 1 mg); a spectrophotometer and a set of cells for ultraviolet radiation; pipettes.

The total amount of the solution to be prepared depends on the volume and the number of vials that will be used in the field experiment. The loss associated with the determination of the concentration and vial-filling should also be considered. The numbers of vials should include those for the control (without exposure) and for the measurement of I₀. A number of vials amounting to 5 to 10% of the total number of vials is suitable for the control.

The required amount of anthracene (a solid substance) is roughly weighed with a balance. Anthracene is dissolved in alcohol in a bottle placed under dark conditions by mixing with the magnetic stirrer for about one day. The bottle must be wrapped to avoid evaporation of alcohol. After complete dissolution of anthracene, the concentration of the solution is checked by measuring the absorbance.

3) Filling vials with the solution

Instruments: Vials (the type used in the following experiment is the 4 ml screw vial S-1, Nichiden-rika-garasu, 15 mm in diameter and 45 mm in height) with cap packings (polyethylene cap packings are recommended because they are insoluble in ethyl alcohol, airtight and economical); containers (to hold the vials); an autoburet or a dispenser (convenient for preparing a large number of vials).

The vials are filled with the solution. Although the exposure of the solution to room light does not affect appreciably the concentration, it is preferable to keep the exposure to a minimum. The time required for filling and capping should be short to avoid evaporation. When rubber bands or other instruments are used for setting the vials in the field, they should be placed on the vials at this stage. Until exposure in the field, the vials must be stored in lightproof containers or in a dark room. The solution in the vials can be maintained at a constant concentration in the dark for a long period of at least several months.

4) Field measurement

For measuring the relative radiation, the vials containing the anthracene solution are placed in targeted positions in the plant canopy. Vials are also located outside the canopy for determining I₀ (100% relative radiation) and in a lightproof box for control (0% relative radiation). The vials inside and outside the canopy must be set using the same tools and in the same way.
To measure the light environment during a whole day, the vials should be set before sunrise and collected after sunset. When it is impossible to set the vials before sunrise, they can also be set in the daytime and removed on the next day at the same time. When the setting takes a long time or the weather conditions rapidly change during the setting, it is recommended to place several $I_0$ sets corresponding to the vials that are placed inside the canopy at different times. After retrieving the vials, they must be kept in a lightproof box or in the dark.

5) Measurement of absorbance for each vial

Absorbance is measured after keeping the vials without disturbance for at least about one day to enable dianthracene to settle at the bottom of the vials. The top clear part of the solution in a vial is transferred to a cell, and the absorbance is measured. Relative radiation is calculated by Eq.(4) based on the absorbance of $I_0$ and the control.

Examples of field measurements

1) Measurement of light conditions for sub-canopy trees in multiple-layered forests

Using the anthracene method, the light conditions of the trees in a lower canopy layer of Chamaecyparis obtusa forests were measured for analyzing the relationship between the light conditions and tree growth. The forests were characterized by a multiple-layered canopy structure. In five stands located on the western slope of Mt. Tsukuba, Japan, the relative radiation just above the lower trees and their size were measured. The stand consisted of different stem densities of upper layer trees and an identical density of lower layer trees.

The initial concentration of the anthracene-ethyl alcohol solution was about 6 mg/l and

Fig. 2. Relationship between the relative radiation and the mean annual increment of lower layer trees in multiple-layered forests

Schematic drawing shows the setting conditions of the experiment.
the wavelength at which the absorbance was measured was 356.8 nm. The solution was divided into 4 ml vials (Nichiden-rika-garasu). In one plot, 60 vials were placed on strings, 1.2 mm in diameter, with rubber bands attached to the vials. The vials were set just above the top of the lower trees at a height in the range of 2.5–5 m, utilizing the stems of the upper layer trees (Fig. 2). The vials were placed in the daytime on 4 September, 1992, and were collected on the next day at the same time as the setting. It was cloudy on both days with

![Fig. 3. Vertical and horizontal distribution patterns of the relative radiation in a Japanese larch forest.](image-url)
occasional sunshine. Fig. 2 shows the relationship between the relative radiation and the annual growth rate of each organ of individual trees, indicating that the annual growth rate increased with the increase in relative radiation.

2) Vertical radiation distribution in a Japanese larch forest

Vertical patterns of the relative radiation were observed with the corresponding profile of leaf biomass density in a 17 years old Larix kaempferi plantation\(^6,7\). The stand density was about 2,500 trees/ha and the mean tree height was about 10 m. Vials (same type as those used above), each containing 4 ml solution, were set among three larch stems at heights between 9.3 and 1.3 m above ground (Fig. 3). Strings and rubber bands were used for building the apparatus. Sixty vials were placed between two stems for each height level. Field experiment was conducted in August. Although the initial concentration of the solution was as high as 30 mg/l, the extent of the change (reduction) in concentration (caused by the photochemical reaction) remained within an acceptable range of linearity, due to the cloudy condition. The locations of the vials were recorded when they were collected. After the vials were removed, their absorbance was determined using a digital spectrophotometer at the wavelength of 350 nm. Fig. 3 shows the relative radiation along the positions within the canopy. Relative radiation was lower near the stems, and higher in intermediate positions between the stems. Light extinction coefficient\(^10\) was estimated at 0.46 ha/ha from the cumulative leaf area density and the vertical distribution of relative radiation.

Further considerations about the method

One of the potential problems of the anthracene method could arise in the determination of the concentration. The concentration of anthracene is closely related to the maximum radiation that can be measured and to the sensitivity to solar radiation. First, care must be taken so that the measurements are performed in the range below the maximum radiation value. As a result, under high solar radiation, the concentration should be low. However, since a solution at a low concentration shows a low sensitivity, small differences in radiation among positions may not be detectable in darker places (e.g. forest floor). This problem can be overcome using two levels of concentration. Two approaches can be considered.

The relationship between the coefficient \(\mu\) and the initial concentration \(A\) in Eq.(2) can be approximated, within the range between \(A = 5\) and 40 mg/l, by a power function as\(^3\):

\[
\mu = g \ A^h, \ .................................. (5)
\]

where \(g\) and \(h\) are coefficients\(^3\). The value of \(h\) was estimated at 0.423. When the solution with a low concentration (initial concentration is \(A_1\)) is set outside the canopy, and a solution with a high concentration (initial concentration is \(A_2\)) is set inside the canopy, the relative radiation inside the canopy \(I'/I_0\) is calculated as:

\[
I'/I_0 = (A_1/A_2)^h \frac{\ln (A_2/C_2)}{\ln (A_1/C_1)}, \ ........ (6)
\]

where \(C_1\) and \(C_2\) are the concentrations of residual anthracene in the solution exposed outside and inside the canopy, respectively. It is preferable to determine the \(h\) value under the experimental conditions, as \(h\) is an important variable for the calculation of the relative radiation from Eq.(6).

The other method is based on the utilization of the measurements in an intermediate position. Vials containing a solution with a low concentration are set outside the canopy and in the intermediate position, while vials with a solution at a high concentration are set in a dark targeted position and in the same intermediate position. Relative radiation \(I'/I_0\) is calculated by the formula:
where $I_{M}/I_{0}$ is the relative value of radiation in the intermediate position to that outside the canopy. Similarly, $I'/I_M$ is the relative value of radiation in the targeted position to that in the intermediate position.

The other problem to address is related to the chemical characteristics of anthracene which reacts mostly with ultraviolet radiation. In the application of the method it is assumed that the relationship between the integrated radiation and the concentration of anthracene does not change inside and outside the canopy. Although the regression of Eq.(1) is derived on the basis of the relationship between the concentration and photon flux density, illuminance, or total irradiance outside the canopy, in some cases the relationship may not be applied within the canopy. For analyzing the light environment in more detail, the assumption should be tested carefully.

Various apparatus can also be developed for use in different field experiments. We described a method using vials, strings and rubber bands. Although the vials were located with their caps upward, it is likely that the caps intercepted only part of the radiation coming from above due to the nearly continuous swing of the vials. Methods can be developed using other instruments which are more suitable for particular conditions and can be applied to various measurements of the light environment.

References


(Received for publication, Feb. 4, 1993)