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Photolysis Rate of Aqueous Solution of Naproanilide, 2-(2-Naphthoxy)propionic Acid and Chlornitrofen Exposed to Outdoor Sunlight

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As we have reported monthly means of the sunlight UV energy in the FRA-greenhouse, monthly mean of the outdoor UV energy can be estimated from the relationship between outside UV intensity and UV intensity inside the FRA-greenhouse. In our measurement UV intensity on the outside was two times higher than UV intensity inside FRA-greenhouse in Chigasaki city. Thus the outdoor UV energy was estimated two times higher than the UV energy inside the FRA-greenhouse. In this way, the outside UV energy could be estimated by using this relation. We investigated the quantitative photolysis rate of aqueous solution of naproanilide (2-(2-naphthoxy)propionanilide), NOP (2-(2-naphthoxy)propionic acid) and chlornitrofen (2,4,6-trichlorophenyl 4-nitrophenyl ether) exposed to outdoor sunlight. The results showed that photolysis rate of naproanilide fitted to the exponential function, and its PL_{50} value on the outside was the same as that inside the FRA-greenhouse. Delaying phenomenon was detected in the initial photolysis of NOP and chlornitrofen. It is not clear how they occur, so far. A probable reason is that another material is activated by the light and this activated material makes an opportunity for the photolysis of NOP and chlornitrofen. Once the reaction started, however, the photolysis rate approximated to an exponential function.

INTRODUCTION

Half-life is not reproducible under different conditions because it has been thought photostability depend on the time of sunlight irradiation. The intensity of sunlight irradiation constantly changes. So, we have been reported that the reproducible and quantitative photolysis rate can be determined by the relationship between the decomposition of a pesticide and the UV energy at the sample surface.

It is not known the scattering and the transmittance of irradiation in a range of about 300 nm inside the FRA-greenhouse. The photolysis rates of naproanilide (2-(2-naphthoxy) propionanilide) exposed to a xenon lamp and exposed to sunlight in the FRA-greenhouse have been reported,[1,2] but its rate on the outside has not yet been reported. So it is uncertain whether it is possible to get the same results in different experiments. We tried to compare the two rates of naproanilide photolysis inside the FRA-greenhouse and on the outside.

Oyamada & Kuwatsuka[3] have reported the photodegradation of both naproanilide and NOP (2-(2-naphthoxy) propionic acid) on the outside, but their degradation rate conversion per time can not be used to make a comparison between naproanilide and NOP, because their photodegradation procedure are under different conditions of solar irradiation.

There are some reports on the photolysis rate of chlornitrofen (2, 4, 6-trichlorophenyl

4-nitrophenyl ether) and diphenyl ether. Naka-gawa & Crosby have reported[4,5] that nitrofen disappear rapidly in the first week by being ex-posed to sunlight, and that the sunlight photolysis of nitrofen (2, 4-dichlorophenyl 4-nitrophenyl ether) in aqueous methanol represents a photonucleophilic displacement of nitrophenate by the hydroxide ion of water. Choudry et al.[6] have reported the photoreac-tions of a series of chlorinated diphenyl ethers at wavelengths around 300 nm. They investi-gate the photodecomposition rates and products formed. The quantitative photolysis rate of chlornitrofen have not yet been reported.

This paper presents the relationship of UV intensity on the outside to UV intensity inside the FRA-greenhouse and the comparison of the quantitative photolysis rate of aqueous solution of naproanilide, NOP and chlornitrofen exposed to outdoor sunlight. The rate were investigated to determine whether they fitted to the exponential function, and whether it was possible to get the same PL_{50} values of napro-anilide inside the FRA-greenhouse and on a field. And we investigated monthly mean of the outdoor UV energy to estimate the PL_{50} value.

MATERIALS AND METHODS

1. Measurement of UV Intensity

The UV energy below 350 nm is small, as small as a measurement error of the total UV energy at the region of 300 nm to 400 nm. In case of direct photolysis, UV intensity of the wavelength below 340 nm had to be measured, so the UV radio meter (UVR-254: Tokyo Kougaku Kikai K.K.) was used. This instru-ment was very convenient because it was able to measure UV below 340 nm. Many pesti-cides absorb this region of the UV rays. The UV intensity was measured by placing this instrument horizontally at the surface of the samples. Its intensity value was reported under each experimental condition. The ener-gy E (cal/cm²) was calculated by the following equation.

$$E = (W \times t)/4.186$$

Where W was UV intensity (W/cm²), t was irradiation time (sec) and 4.186 was the con-version factor from joule to calorie. Chigasaki,

where this experiment was carried out, was located 139° 31′ E and 35° 29′ N.

2. Preparation of Sample Solution

An excess amount of naproanilide (purity 99.8%) was suspended in distilled water. After standing overnight at 25°C, the suspension was filtered through a filter paper (No. 5C), and the solution was used as saturated aqueous solu-tion.

Water solubility of NOP is 700 ppm (27°C) but it does not become such high concentration in the environment. So, the concentration was set at 7.75 ppm. Lower concentration was not appropriate because of the detection limit of HPLC.

Since chlornitrofen (purity 99.9%) was practically insoluble in water, the excess amount was suspended in 20% methanol in water. After standing overnight at 25°C, the suspension was filtered through filter paper (No. 5C). This solution was used as irradiation samples.

3. Analytical Methods

The sample solution (1 ml) of naproanilide or NOP was taken and 6 ml of methanol was added to these solutions. Concentrations of these solutions were analyzed by HPLC (Shi-madzu model LC-5A) equipped with a fluores-cence spectromonitor (Shimadzu model RF-530, EM wavelength 340 nm, EX wavelength 275 nm) and a chromatographic column packed with Lichrosorb RP-8 (300×4 mm i.d.). The mobile phase consisted of 15% water in metha-nol.

The sample solution (1 ml) of chlornitrofen was analyzed by the same HPLC equipped with a UV monitor. The mobile phase was metha-nol, and detection wavelength was 290 nm.

4. Measurement of Molar Absorptivity Spec-trum

NOP (purity 99.9%) and chlornitrofen (purity 99.8%) were dissolved in methanol, and absorption of these compounds was measured with a spectrophotometer (Hitachi model 220A).

The data of naproanilide was cited from the previous report.[1]

5. Photolytic Procedures

Naproanilide photolysis was carried out by putting the solution into a glass pot (9.5 cm i.d. ×4.5 cm) in direct sunlight on Aug. 20, 1986 at 14:00 and the initial concentration was 0.631 ppm. The NOP photolysis was carried out on Aug. 20, 1986 at 14:00 and the initial concentration was 7.75 ppm. The chlornitrofen photolysis was carried out on Aug. 26, 1986 at 14:13 and the initial concentration was 47.1 ppm. The chlornitrofen photolysis was not completed in one day. So, after the solar altitude became lower than 20°, samples were covered to prevent evaporation, and stored in a dark and cold room. All procedures were carried out on the outside in a glass pot filled with a sample solution.

6. Calculation of Photolysis Rate

The photolysis rate was expressed by the following exponential function.[1,2]

$$Y = Y' \times \exp(-K \times E) \qquad (1)$$

Where Y' was an initial concentration of the pesticide, Y was the concentration of the remaining pesticide, E was sunlight energy (mcal/cm²) and K was photolysis constant. For the purpose of a simplified comparison, Y and Y' in Eq. (1) were replaced by percentages in this report. The PL_{50} value (50% photolysis: cal/cm²) was expressed by the following equation.

$$PL_{50} = 0.693/K$$

RESULTS

1. UV Irradiation of Sunlight

Figure 1 shows daylong variation of UV intensity on a clear day, and Fig. 2 shows daylong variation of the UV intensity on a day that is fair with some afternoon rain. The date of Fig. 2 was the day before Fig. 1, so there was no difference in solar altitudes between the two days. The difference of these figures may have been caused by cloud.

The UV intensity was observed high at 7:00 but weak from 8:00 to 9:00 because of thin cloud, as shown in Fig. 1. UV intensity was changed by thin cloud even on a fine day. Daylong variation of UV intensity was usually like Fig. 2, and the variation like Fig. 1 was very rare in a year. The UV intensity was measured inside and outside the FRA-greenhouse on fine days. The relationship between solar altitude and intensity was mentioned in the discussion.

2. Molar Absorptivity Spectra of Compounds

Figure 3 shows the molar absorptivity spectra of naproanilide, NOP and chlornitrofen. The molar absorptivity of naproanilide and NOP could not be measured at wavelengths of more than 350 nm because of slight solubility in methanol. Figure 3 shows that naproanilide and NOP can absorb UV irradiation below 350
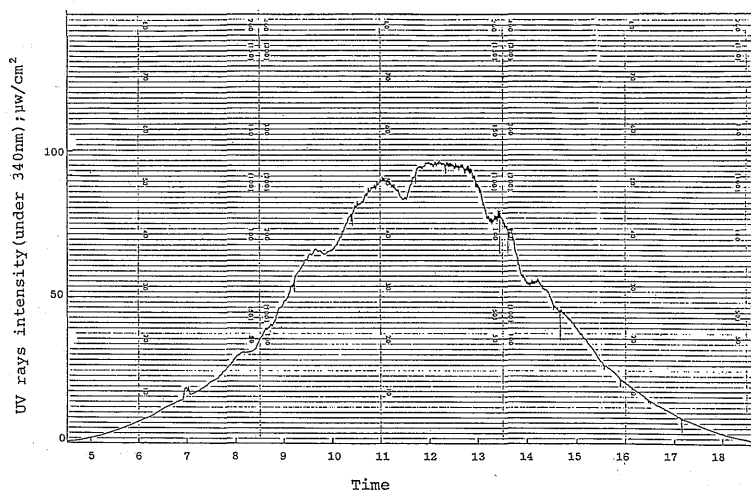

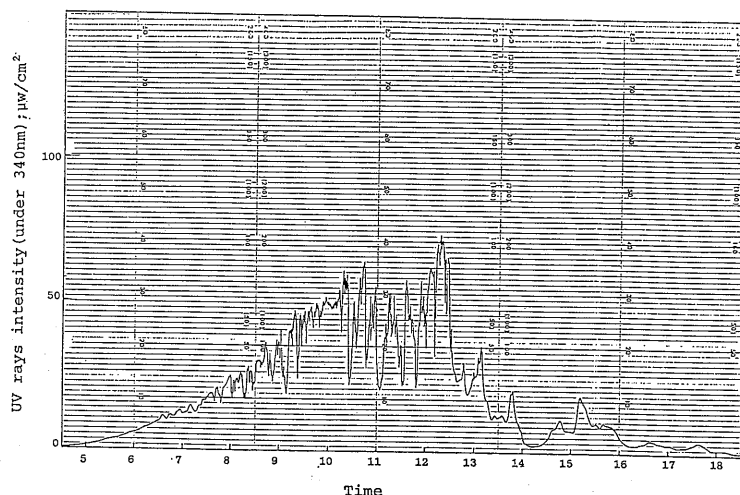Fig. 1 Daylong variation of UV intensity on June 5, 1985.

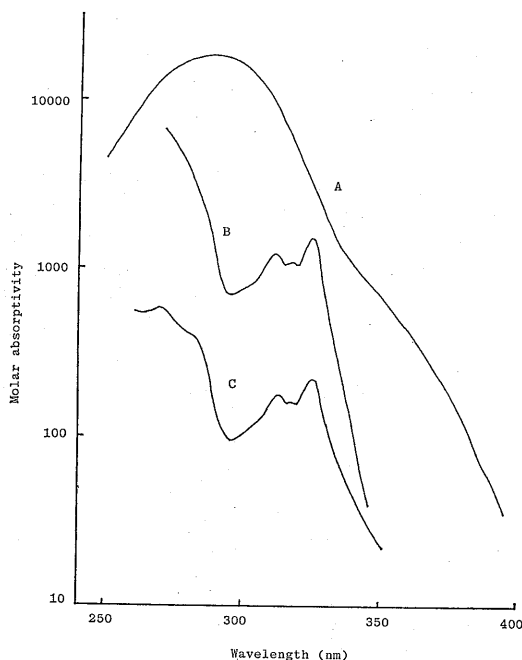Fig. 2　Daylong variation of UV intensity on June 4, 1985.

Fig. 3　Molar absorptivity spectra of naproanilide, NOP and chlornitrofen in methanol.

A, chlornitrofen; B, naproanilide; C, NOP.

nm. In case of chlornitrofen, it showed high absorption in the range of 300 nm to 400 nm.

3.　Photolysis Rate of Compounds Exposed to Outdoor Sunlight

Figures 4, 5 and 6 show the photolysis of naproanilide, NOP and chlornitrofen, respectively. The relationships between the irradiation energy (below 340 nm: mcal/cm²) and the remaining of compound (%) were fitted to Eq. (1) with the Gauss-Newton method as nonlinear least squares, and Eqs. (2), (3) and (4) were obtained. The high values of multiple correlation coefficient R and F-test were determined, so this photolysis rate was approximated by an exponential function (1).

3.1　Naproanilide

The PL_{50} value of naproanilide in this report (Fig. 4) was 12.56 mcal/cm² and similar to the value in the previous report.[1]

$$Y = 105.6 \times \exp(-0.0552 \cdot E) \qquad (2)$$
$$R = 0.994, \ F_{2,13} = 568.5$$
$$PL_{50} \ (\sim 340 \ nm) = 12.56 \ mcal/cm^2$$

3.2　NOP

As shown in Fig. 5, the photolysis of NOP did not occur at first, therefore the energy (5.64 mcal/cm²) of the delayed phenomenon was exempted from the calculation of data. The PL_{50} value of NOP was 4.44 mcal/cm². This means that NOP is more unstable than naproanilide to the light.

$$Y = 98.0 \times \exp(-0.156 \cdot E) \qquad (3)$$
$$R = 0.993, \ F_{2,9} = 313.6$$
$$PL_{50} \ (\sim 340 \ nm) = 4.44 \ mcal/cm^2$$

3.3　Chlornitrofen
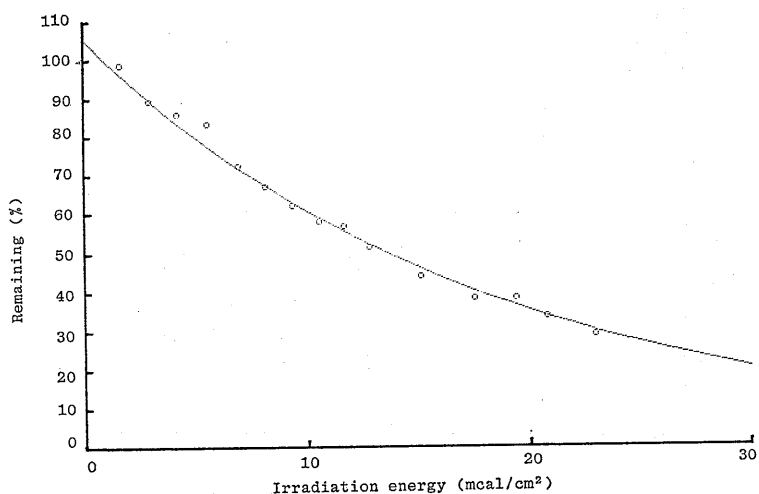
As shown in Fig. 6, the delayed phenomenon

Fig. 4 Photolysis rate of aqueous solution of naproanilide exposed to outdoor sunlight.
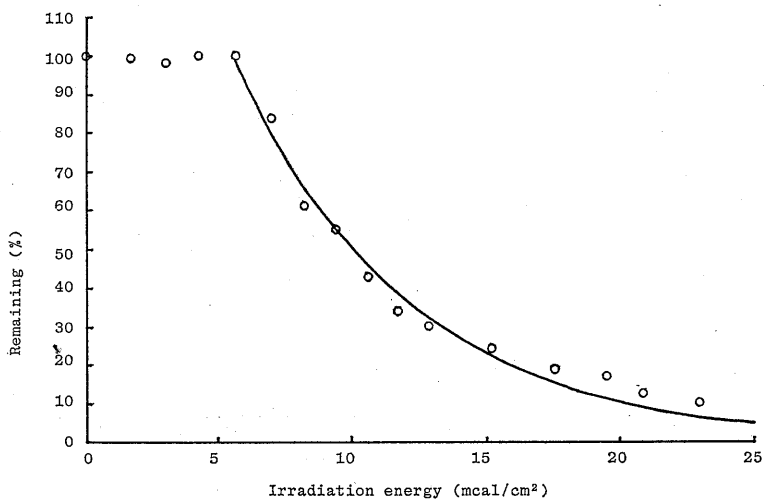

Fig. 5 Photolysis rate of aqueous solution of NOP exposed to outdoor sunlight.

of chlornitrofen was found to be similar to that of NOP. The energy (199.39 mcal/cm²) of the delayed phenomenon was exempted from the calculation of the data. The PL_{50} value of chlornitrofen was 816.7 mcal/cm². This means chlornitrofen is more stable to the light than naproanilide and NOP.

$$Y = 100.7 \times \exp(-0.000849 \cdot E) \quad (4)$$
$$R = 0.978, \ F_{2,3} = 33.7$$
$$PL_{50} \ (\sim 340 \ nm) = 816.7 \ mcal/cm^2$$

DISCUSSION

1. UV Intensity and Solar Altitude

Figure 7 shows the relationship between UV intensity (below 340 nm) and solar altitude, and these data were cited from fine day's data like Fig. 1. The vertical axis is the UV intensity (below 340 nm) inside the FRA-greenhouse or on the outside on a fine day during the last three years. The horizontal axis is the solar altitude at that time. There are
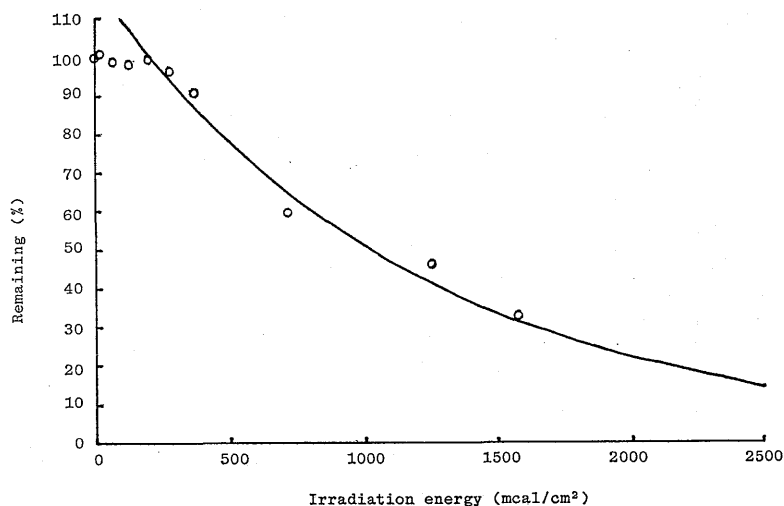
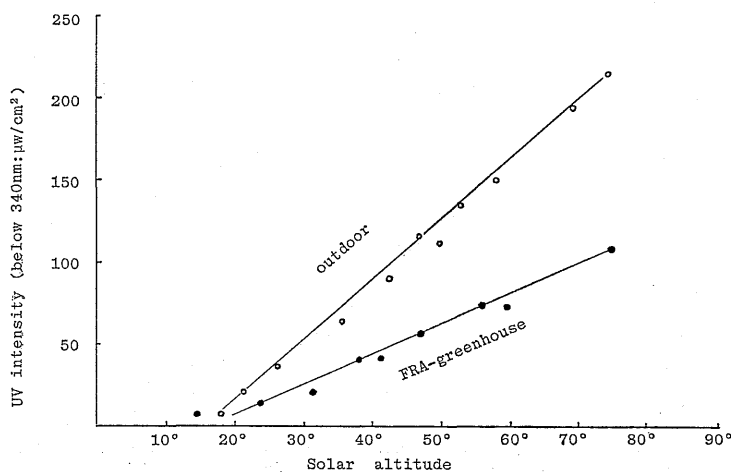Fig. 6　Photolysis rate of aqueous solution of chlornitrofen exposed to outdoor sunlight.

Fig. 7　Relationship between solar altitude and UV intensity (below 340 nm).

slight variations like Fig. 7 on a fine day though, because UV intensity (below 340 nm) is easily affected even by thin cloud. The points beneath the line of maximum intensity in Fig. 7 were not included because their values were lowered by cloud. Therefore, the line is composed of maximum UV intensity at some solar altitudes. Figure 7 showed that UV intensity (below 340 nm) increased in proportion to the increase of solar altitude. As a result, it was clarified that UV intensity (below 340 nm) was two times stronger on the outside than inside of the FRA-greenhouse. Monthly

means of the UV energy (below 340 nm) for the year in the FRA-greenhouse have already been reported.[1] In terms of energy, the outdoor UV energy (below 340 nm) was two times greater than UV energy (below 340 nm) inside the FRA-greenhouse. The outside UV energy will be able to be estimated by using this relationship.

There was a nonlinear relationship between the UV intensity and the solar altitude below 20°. One of the reasons was that the detector was placed horizontally to measure sun irradiation and sky irradiation. This means photoly-
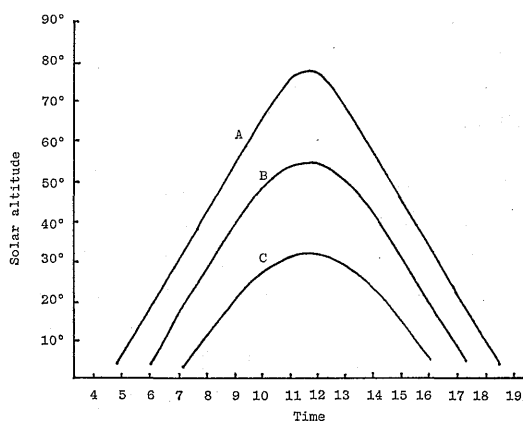
Fig. 8   Change of the solar altitude in Chigasaki.

A, summer solstice; B, vernal equinox, autumnal equinox; C, winter solstice.

sis is determined exactly with a UV radio meter UVR-254 under the same condition of the solar altitude is more than 20° or less than 20°. Figure 8 shows the calculated change of solar altitude at Chigasaki city. If there is no cloud, UV intensity will be exactly observed like Fig. 8 because of the relationship shown in Fig. 7. The solar altitude has to be checked each test to do more than 20° solar altitude. The solar altitude is more than 20° from 9:00 to 14:30 on the winter solstice in Chigasaki. It is also more than 20° from 7:00 to 16:00 at the vernal equinox and from 6:00 to 17:30 at the summer solstice in Chigasaki.

2. The Photolysis Rates of Three Compounds

The photolysis rates of naproanilide in the FRA-greenhouse have been reported.[1] FRA plastic (glass fiber reinforced polymethyl methacrylate sheet: Mitsui Toatsu Chemicals, Inc.) transmits UV rays, but it is not clear scattering and transmittance of around 300 nm irradiation in the FRA-greenhouse. So, the photolysis rate of naproanilide was investigated to compare the difference of the photolysis rate between the inside and the outside. The photolysis rate of naproanilide exposed to the outdoor sunlight could be simulated by an exponential function like Eq. (1). Equation (2) showed high values of multiple correlation coefficient and F-test, and this relation seemed to be a pseudo first-order reaction. The PL_{50}

value was 12.56 mcal/cm², which was similar to the PL_{50} value inside the FRA-greenhouse, 9.5–11.1 mcal/cm².

The delayed phenomenon was identified on the initial photolysis of NOP and chlornitrofen. It is not clear how they occur, so far. A probable reason is that another material is activated by the light, and this activated material makes an opportunity for the photolysis of NOP and chlornitrofen. The energy needed by this agent is different under each condition (Other data are not shown in this report). After starting of the reaction, the photolysis rate approximated to the exponential function.

Chlornitrofen had the strongest absorption of all, but its photolysis rate was the slowest. Conversely, NOP had the weakest absorption and the weakest photostability. These results showed that the absorption of the sunlight was needed for photolysis, but the photostability could not be explained by absorbance alone. Therefore it was possible to compare stability to the sunlight when the photostability was explained by both the absorption and the quantum yield. The product of molar absorbance and quantum yield, namely, the photolysis constant K of Eq. (1) will be a satisfactory parameter.

ACKNOWLEDGMENTS

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要　　約

ナプロアニリド，2-(2-ナフトキシ) プロピオン酸および CNP 水溶液の屋外太陽光による光分解

船越安信，江田貞文，南保俊夫
榊原昌弘，日比佐知子

　屋外太陽光によるナプロアニリド (2-(2-naphthoxy) propionanilide)，NOP (2-(2-naphthoxy) propionic acid)，CNP (2,4,6-trichlorophenyl 4-nitrophenyl ether) の光分解率を時間ではなく，時間と紫外線強度の積である紫外線エネルギー (cal/cm²) で捉えると紫外線強度の変化する太陽光であっても指数関数式で近似できることが明らかとなった．ナプロアニリドの PL_{50} 値は FRA 樹脂温室内のデータと同じであり再現性があった．一方，NOP，

CNP の光分解では遅延現象が認められた．　しかし，反応が始まると指数関数式に適合した．この遅延現象の原因の一つとして，使用した蒸留水に含まれているなんらかの物質が始めに光で活性化されそれがその後の光分解を引き起こしたことも考えられる．光安定性の指標である PL_{50} 値 (mcal/cm²) が明らかとなっても，屋外での紫外線エネルギー変化(mcal/cm²) が不明では実際にどの程度，光に安定か判断できない．屋外と FRA 樹脂温室内の紫外線強度 (μW/cm²) を比較し屋外の紫外線強度は FRA 温室内の2倍であることから，屋外の紫外線エネルギー (cal/cm²)は FRA 樹脂温室内の2倍であることが明らかとなった．茅ケ崎市における年間の屋外での太陽紫外線エネルギー変化は，すでに報告されている FRA 樹脂温室内の紫外線エネルギーの年間変化の2倍と考えればよいことが明らかとなった．