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DETERMINATION OF SCALAR IRRADIATION AVAILABLE FOR PHOTOLYSIS IN NATURAL WATERS by

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MANAGEMENT PERSPECTIVE

This work was done to provide chemists and biologists concerned with subsurface photosynthesis and/or photodegradation with a means of determining an accurate estimate of the energy to which a cell or a contaminant is exposed. Previously we have devised an optical model by which the components of vector irradiance may be converted into the more appropriate scalar irradiance. This work significantly extends the model by enabling the daily integrated values of the downwelling irradiance either just above or just below the air/water interface to be directly converted into the subsurface scalar irradiation available for photolysis.

PERSPECTIVE-GESTION

Ces travaux ont été effectués pour fournir aux chimistes et aux biologistes dont les travaux portent sur la photosynthèse et (ou) la photodégradation dans l'eau la possibilité de déterminer précisément l'énergie à laquelle une cellule ou un contaminant est exposé. Nous avons déjà mis au point un modèle optique permettant de transformer les composantes de l'irradiation vectorielle en irradiation scalaire qui constitue une forme plus utile. Ces travaux apportent un complément significatif au modèle en permettant de transformer directement les valeurs intégrées quotidiennes de l'irradiation en plongée immédiatement au-dessus ou audessous de l'interface air-eau en irradiation scalaire utilisée pour la photolyse.

ABSTRACT

Multiplicative factors are derived which enable the conversion of incident radiation (either above or below the air/water interface) into the subsurface daily scalar irradiation available for photolysis. These multiplicative factors are presented as functions of the volume reflectance of the water and illustrate that for volume reflectances in the range 0.0 to 0.14, the actual subsurface daily scalar irradiation available for photochemical and photobiological reactions varies between 1.1 and 2.1 times that value of subsurface daily irradiation generally considered available for such reactions.

RÉSUME

Des facteurs multiplicatifs permettent de convertir le rayonnement incident (au-dessus ou au-dessous de l'interface air-eau) en irradiation scalaire quotidienne disponible pour la photolyse dans l'eau. Ces facteurs multiplicatifs sont présentés sous formes de fonctions de la réflexion volumique de l'eau et montrent que pour des réflexions volumiques de l'ordre de 0,0 à 0,14, l'irradiation scalaire quotidienne réelle dans l'eau, qui peut être utilisée pour les réactions photochimiques et photobiologiques, varie de 1,1 à 2,1 fois la valeur de l'irradiation quotidienne généralement considérée disponible pour de telles réactions.

INTRODUCTION

A realistic evaluation and understanding of the photolysis (photochemical and photobiological reactions) occurring in natural waters requires precise knowledge of the actual energy density to which the chemical or biological aquatic component is exposed. Such energy density information is crucial to any estimation of the rates at which these reactions occur. The standard meteorological measurement (or meteorological model prediction) is the incident global radiation either with or without the differentiation between its direct and diffuse components. Global radiation, however, is a measure of the downwelling irradiance, and therefore, possesses inherent geometric properties. These geometric features, related to the arrival directions of the impinging radiation, are incorporated into the directly measured or inferred values of the global radiation. Consequently. subsurface downwelling irradiances determined from such global radiation values contain corresponding directional biases. As such, subsurface downwelling irradiance is not the appropriate parameter to consider in the study of photochemical or photobiological processes. Rather, the appropriate parameter for photolysis is the scalar irradiance which does not incorporate directional biases into its definition. The scalar irradiance is the total energy per unit area arriving at a point from all directions when all directions are equally weighted, and, when divided by the speed of light in water, readily yields the actual energy density at that point.

Jerome et al. (1988) provides relationships between the scalar irradiance E_0 and the downwelling irradiance E_d in natural waters as a function of volume reflectance R, solar zenith angle 0, and depth Z [i.e., relationships between E_0 (Z, θ ,R) and E_d (Z, θ ,R). Despite the awareness that the scalar and downwelling irradiances are indeed functions of Z, θ , R, as well as wavelength λ , these functional dependencies will not be specifically designated beyond this point in the text in order to simplify the notation of the ensuing mathematical formulations. The scalar and downwelling irradiances will be designated as E_0 and E_d , respectively, with the parametric dependencies fully implied]. It was found that the scalar irradiance, at a given depth under certain conditions, could be greater than double the downwelling irradiance at that depth. Similar analyses by Madronich (1987) indicated that scalar irradiance (actinic flux) in the atmosphere can also be much greater than the downwelling irradiance for cloudy conditions and/or high ground albedos. Clearly, therefore, the use of downwelling irradiances can result in significant underestimations of the rates of photochemical and photobiological processes occurring in both the atmosphere and natural waters.

This manuscript presents a means of obtaining subsurface irradiation (i.e., time integrated irradiance) appropriate for photolysis. In order to obtain such irradiation values a set of multiplicative factors will be derived which can be directly applied to values of incident radiation. The incident radiation under

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consideration may be a downwelling irradiance as a function of time $(1.e., \theta)$ or a daily irradiation. These incident radiation values are determined from either direct measurements or solar irradiance models such as used by Zepp and Cline (1977).

For the analyses described herein, the only hydro-optical parameter required is the water's volume reflectance $R(0^{\circ})$ (ratio of upwelling to downwelling irradiance just below the surface for a solar zenith angle of zero degrees. Since volume reflectance is a function of wavelength, the wavelength dependencies of the photolysis are satisfied by selecting the appropriate values of $R(0^{\circ})$ and the incident radiation at each wavelength).

The methodology by which the multiplicative factors are determined is outlined in Figure 1. The three inter-related activities depicted therein may be described as follows:

a) For a chosen water type [defined by its volume reflectance R (0°)] and an incident above-surface radiation (defined by the solar zenith angle θ), a Monte Carlo photon propagation simulation was utilized to determine the ratio E_0/E_d as a function of Z, θ , and R [designated as D (Z,θ,R)]. This ratio of subsurface scalar irradiance to subsurface downwelling irradiance was then depth integrated to obtain $\sum_{T} D(\theta,R)$.

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- b) An air/water interface transmission analysis, along with appropriate boundary conditions, was used to obtain the ratio of the downwelling irradiance just below the surface E_d^- to the downwelling irradiance just above the surface E_d^+ . (The functional dependence of E_d^- and E_d^+ on θ and R are implicit in the E_d^- and E_d^+ nomenclature.)
- c) A global radiation model was used to provide an appropriate expression for E_d^+ . This value of E_d^+ was used in conjunction with the ratio E_d^-/E_d^+ to yield E_d^- .
- d) The expressions for $\sum_{Z} D(\theta, R)$, E_d^{-}/E_d^{+} , and E_d^{-} obtained from steps a), b), and c), were then mathematically synthesized and integrated over the daylight period to obtain the multiplicative factors $\sum_{\Theta Z} D^{-}(R)$ and $\sum_{\Theta Z} D^{+}(R)$. These multiplicative factors may then be used to convert subsurface and above-surface daily irradiation, respectively, into subsurface daily scalar irradiation available for photolysis.

These multiplicative factors will be displayed as a function of the volume reflectance of the natural water mass for both direct and diffuse incident radiation distributions for specific seasons and latitudes. DEPTH INTEGRATION OF THE RATIO OF SCALAR IRRADIANCE TO DOWNWELLING IRRADIANCE

From the Monte Carlo simulation of photon propagation in natural waters as described in Jerome <u>et al</u>. (1988), the ratio of the subsurface scalar irradiance E_0 to the subsurface downwelling irradiance E_d was determined at depths Z where the downwelling irradiance was equal to 1.0, 0.8, 0.5, 0.25, 0.1, and 0.01 of its value just below the surface. These ratios were obtained for direct beams incident at solar zenith angles θ of 0°, 30°, 60°, and 89°, as well as for a diffuse cardioidal distribution. Fifteen distinct water types characterized by volume reflectances between 0.0 and 0.14 were considered. The ratio E_0/E_d is defined by $D(Z,\theta,R)$ as indicated in Figure 1.

Curve-fitting was performed on the six depth values of $D(Z,\theta,R)$ to obtain the depth dependencies (as shown in Figure 2 for $R(0^\circ) = 0.08$) for each of the possible θ and R combinations. The curves were then integrated over depth according to

 $\sum_{Z} D(\theta,R) = \frac{\sum_{z_1}^{z_2} D(Z,\theta,R) E_d Z}{\sum_{z_1}^{z_2} E_d Z}$

(1)

where $\sum_{Z} D(\theta,R)$ = the depth integrated value of the ratio of the scalar irradiance E₀ to the downwelling irradiance E_d.

> Z_1 = depth of the 1% downwelling irradiance level Z_2 = depth of the 100% downwelling irradiance level

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 $\sum_{Z} D(\theta,R)$ is the average value of the ratio E_d/E_0 down to the photic depth for a particular θ and R. That is, over the photic zone the scalar irradiance is, on average, the product of the factor $\sum_{Z} D(\theta,R)$ and the downwelling irradiance. Discrete values of $\sum_{Z} D(\theta,R)$ resulting from equation (1) are shown as a function of $R(0^{\circ})$ in Figure 3 for the five incident radiation distributions considered.

In order to obtain explicit mathematical relationships among $\sum_{Z} D(\theta,R)$, θ , and R, the values of $\sum_{Z} D(\theta,R)$ as a function of R were z curve fitted for each incident radiation distribution to a polynomial expansion series of the form

$$\sum_{Z} D(\theta, R) = \frac{1}{\mu_0} \left[1 + c_1 R(0^\circ) + c_2 R(0^\circ)^2 + c_3 R(0^\circ)^3 \right]$$
(2)

where

 $\mu_0 = \cos [\sin^{-1} (n \sin \theta)]$

n = relative refractive index of water

 c_1 , c_2 , and c_3 = constants

Values of the constants c_1 , c_2 and c_3 resulting from the curve fitting are listed in Table 1 for θ values of 0°, 30°, 60°, and 89°. Prieur and Sathyendranath (1981) have shown that an incident diffuse cardioidal distribution produces subsurface irradiances similar to those for a direct beam incident at a solar zenith angle of 43°. Consequently, Table 1 also includes c_1 , c_2 and c_3 values for a solar zenith angle $\theta = 43°$ which are taken to be equivalent to those for an incident diffuse cardioidal distribution. The continuous curves of Figure 3 illustrate the relationships resulting from the curve-fitting superimposed upon the discrete $\sum_{Z} D(\theta,R)$ values obtained from equation (1). The maximum difference between the discrete values of $\sum_{Z} D(\theta,R)$ and the predictions of equation (2) for all incident radiation distributions considered is less than 1.0%.

Thus, equation (2) readily provides the R dependence of $\sum_{Z} D(\theta,R)$ for five distinct solar zenith angles. To obtain the θ dependence for those intermediate θ values not specifically shown in Figure 3, an interpolation equation may be established. Jerome <u>et al</u>. (1988) have shown that the variation of $D(Z,\theta,R)$ with θ is proportional to the change in μ_0^{-1} . Similarly, the interpolation equation for $\sum_{Z} D(\theta,R)$ may be expressed in the form

$$\sum_{Z} D(\theta,R) = \sum_{Z} D(\theta_{1},R) + \left(\frac{\mu_{1}-\mu_{0}}{\mu_{0}}\right) \left(\frac{\mu_{2}}{\mu_{1}-\mu_{2}}\right) \left[\sum_{Z} D(\theta_{2},R) - \sum_{Z} D(\theta_{1},R)\right] (3)$$

where

 θ = any solar zenith angle between 0° and 89° θ_1 and θ_2 = those values of the five solar zenith angles considered in Figure 3 which are immediately less than and greater than the value of θ , respectively (ie., $\theta_1 < \theta < \theta_2$) μ_0 = cos [sin⁻¹ (n sin θ)] μ_1 = cos [sin⁻¹ (n sin θ_1)] μ_2 = cos [sin⁻¹ (n sin θ_2)]

n = relative refractive index of the water

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Clearly, if the value of the subsurface downwelling irradiance E_d^- (value at Z = 0 and just below the air/water interface) is known, then equation (3) yields the factor by which E_d^- must be multiplied to obtain the scalar irradiance E_0 to which the photic zone is exposed. To obtain the value of E_d^- , it is necessary (see Figure 1) to obtain a value of above surface downwelling irradiance E_d^+ (value at Z = 0 and just above the air/water interface) and adjust it for the transmissions and reflections of the air/water interface.

DETERMINATION OF THE DOWNWELLING IRRADIANCE JUST BELOW THE SURFACE

By applying appropriate boundary conditions to the air/water interface it may be readily shown that

$$E_{d}^{-} = \left[1 + \frac{R(\theta)\rho_{u}(\theta)}{1 - R(\theta)\rho_{u}(\theta)}\right] \left[1 - \rho_{d}(\theta)\right] E_{d}^{+}$$
(4)

and

$$A(\theta,R) = \rho_{d}(\theta) + [1 - \rho_{u}(\theta)] \left[\frac{R(\theta)(1 - \rho_{d}(\theta))}{1 - R(\theta)\rho_{u}(\theta)} \right]$$
(5)

where $A(\theta,R) = albedo of the water$

 $\rho_d(\theta)$ = above-surface reflection of downwelling irradiance

 $\rho_{\rm U}(\theta)$ = subsurface reflection of upwelling irradiance

Jerome et al. (1988) have shown that

$$\rho_{\rm H}(\theta) = 0.271 + 0.249/\mu_{\rm c}$$

for clear skies and

$$\rho_{..} = 0.561$$

for an incident diffuse cardioidal distribution.

Clear sky values of $\rho_d(\theta)$ may be determined from Fresnel's equation, while the ρ_d value for an incident diffuse cardioidal distribution may be taken as 0.066 (Jerlov, 1976).

Further, [Jerome et al. (1988)]

$$R(\theta) = \frac{R(0^{\circ})}{\mu_0}$$

for clear skies and

 $R = 1.165 R(0^{\circ})$

for an incident diffuse cardioidal distribution.

Using equations (6), (7), (8), and (9) in conjunction with equations (4) and (5), the ratio of the subsurface downwelling irradiance E_d^- to the above-surface downwelling irradiance E_d^+ along with the albedo may be obtained for any given water type of volume reflectance R(0°).

(8)

(9)

(6)

(7)

Having thus obtained E_d^- as a function of E_d^+ , it remains to select an appropriate diurnal variation for E_d^+ . Conditions of both direct incidence and overcast conditions were considered and their influence on the integration of $\sum_{Z} D(\theta,R)$ over the daylight period are presented below.

DAILY INTEGRATED VALUES OF
$$\sum_{Z} D(\theta,R)$$

(a) <u>Direct Incident Radiation</u>

A global radiation model was taken from Kondratyev (1969) wherein the downwelling irradiance incident at the earth's surface for clear sky conditions is given by

$$E_{d}^{+} = \frac{(2 - \sec \theta) E_{ext} \cos \theta}{2(1-A) - (\sec \theta - 2A)e^{f(\sec \theta - 2)}}$$
(10)

where $E_{ext} = extraterrestral irradiance$

A = albedo A(θ ,R) as defined in equation (5)

f = an atmospheric variable

Monthly values of f are provided in Kondratyev (1969) as a function of latitude. Subsequent analysis in this communication were performed for 4 days (the spring and fall equinoxes and the winter and summer solstices) and 2 latitudes (40°N and 50°N, a latitude range appropriate to the Great Lakes).

Figure 4 illustrates these relationships resulting from equation (10). The E_d^+ values for the equinoxes were identical and are labelled spring/fall in the figure. The differences between the results for 40°N and 50°N were small, and consequently the results for the two latitudes were averaged (<4.5% difference between the averaged value and either unaveraged value).

Two multiplicative factors will now be determined. The first factor $\sum_{\Theta \in Z} D^-(R)$ is designed to convert a subsurface daily irradiation into a subsurface daily scalar irradiation. The second factor $\sum_{\Theta \in Z} D^+(R)$ is designed to convert an above-surface daily irradiation $\Theta \in Z$ into a subsurface daily scalar irradiation. The factors differ in that $\sum_{\Theta \in Z} D^+(R)$ incorporates the transmissions and reflections associated with the air/water interface.

The factor $\sum_{\Theta Z} \sum_{Z} D^{-}(R)$ was determined by first obtaining an ΘZ appropriate time-dependent E_d^+ from equation (10). A corresponding E_d^- was then obtained from E_d^+ using equation (4). $\sum_{Z} D(\Theta,R)$ was then integrated over the daylight period by:

$$\sum_{\theta \in Z} \sum_{z} D^{+}(R) = \frac{\int_{1}^{\theta_{2}} \sum_{z} D(\theta, R) E_{d} d\theta}{\int_{1}^{\theta_{2}} E_{d} d\theta}$$

(11)

where θ_1 = solar zenith angle at sunrise

 $\theta_2 =$ solar zenith angle at sunset

The factor $\sum_{R \in T} D^+(R)$ was determined in a similar manner. Here again, an appropriate time-dependent Ed⁺ was obtained from equation (10). Equation (11) was then used to obtain the corresponding time-dependent E_d^- . incorporate To into the multiplicative factor the transmissions and reflections occurring at the air/water interface, $\sum_{7} D(\theta,R)$ was multiplied by the ratio E_d^{-}/E_d^+ and integrated over the daylight period by:

$$\sum_{\Theta \in Z} D^{+}(R) = \frac{\theta_{1}^{\int_{Q}^{\Theta_{2}}} \left[\sum_{Z} D(\Theta, R)\right] E_{d}^{-} \frac{E_{d}^{-}}{E_{d}^{+}} d\Theta}{\theta_{1}^{\int_{Q}^{\Theta_{2}}} E_{d}^{-} d\Theta}$$
(12)

Using the E_d^{-/E_d^+} relationship of equation (4), equation (12) may be rewritten as:

$$\sum \sum D^{+}(R) = \frac{\theta_{1} \sum D(\theta, R) \left[1 + \frac{R(\theta)\rho_{u}(\theta)}{1 - R(\theta)\rho_{u}(\theta)}\right] \left[1 - \rho_{d}(\theta)\right] E_{d}^{-} d\theta}{\theta_{1}}$$
(13)

Figure 6 illustrates the results of equation (13). Herein is plotted the multiplicative factor $\sum_{\substack{\Theta \\ \Theta \\ R}} \sum_{\substack{D \\ \Theta \\ R}} D^+(R)$ as a function of R for the solstices and the spring/fall equinoxes. The multiplicative factor for the condition of an incident cardioidal distribution (labelled "diffuse") is also shown.

(b) **Overcast Conditions**

For the condition of the incident radiation being appropriately defined throughout the entire daylight period by a diffuse cardioidal distribution, the solar zenith angle dependence is eliminated from all the parameters except E_d^- and E_d^+ . Consequently, $\sum_{Z} D(\theta,R)$ may be rewritten $\sum_{Z} D(R)$ and taken outside the integral sign in equations (11) and (13).

Therefore, the governing equations for an incident diffuse cardioidal distribution become

$$\sum_{R \in Z} D^{-}(R) = 1.164 \left[1 + c_1 R(0^{\circ}) + c_2 R(0^{\circ})^2 + c_3 R(0^{\circ})^3\right]$$
(14)

$$\sum_{\theta \in Z} D^{+}(R) = [0.934 + \frac{0.610R(0^{\circ})}{1 - 0.654R(0^{\circ})}] \sum_{\theta \in Z} D^{-}(R)$$
(15)

where the constants c_1 , c_2 and c_3 are appropriately chosen from Table 1. The curves resulting from equations (14) and (15) are labelled "diffuse" in Figures 5 and 6, respectively. It is seen that the "diffuse" curve of Figure 5 is, of course, identical to the "diffuse" curve of Figure 3.

DISCUSSION

This manuscript has provided multiplicative factors from which subsurface daily scalar irradiation (governing parameter for photolysis) may be determined for any of four possible sets of circumstances, once a particular volume reflectance $R(0^\circ)$ defining the water type is either known, or may be assumed. These four sets of circumstances are:

- a) The downwelling irradiance E_d^+ is known as a function of time (i.e., as a function of θ).
- b) The downwelling irradiance E_d^- is known as a function of time (i.e., as a function of θ).
- c) The daily integrated value of the downwelling irradiance E_d^+ is known.
- d) The daily integrated value of the downwelling irradiance Ed⁻ is known.

For circumstances (a) and/or (b), readers may perform their own time integrations according to the following protocol:

- i) For each solar zenith angle θ at which an E_d^+ or $E_d^$ value is known, equation (3) is used to obtain the corresponding value of $\sum D(\theta, R)$ for a particular water type $R(0^\circ)$.
- 11) If the known values are E_d^+ , then the corresponding values of E_d^- must be obtained from equation (4).
- iii) Once the $(\sum_{Z} D(\theta, R), \overline{E}_{d}^{-})$ data sets are assembled, the subsurface daily scalar irradiation is obtained by performing the integration $\int_{\theta_{1}}^{\theta_{2}} [\sum_{Z} D(\theta, R)] E_{d}^{-} d\theta$

For circumstance (c), Figure 6 may be directly utilized to obtain the appropriate value of $\sum_{\substack{\theta \in Z \\ \theta \in Z}} D^+(R)$. The known daily integrated value of E_d^+ is then multiplied by this factor to obtain the subsurface daily scalar irradiation.

For circumstance (d), Figure 5 may be directly utilized to obtain $\sum_{i=1}^{n} \sum_{j=1}^{n} D^{-}(R)$. The known daily integrated value of E_{d}^{-} is then Θ_{i}^{-} multiplied by this factor to obtain the subsurface daily scalar irradiation.

For example, a volume reflectance of ~6% will necessitate at least a 50% increase in the value of irradiation used for photolysis considerations.

REFERENCES

Jerlov, N.G. 1976. Marine Optics, Elsevier, New York, 231 pp.

Jerome, J.H., Bukata, R.P. and Bruton, J.E. 1988. Utilizing the components of vector irradiance to estimate the scalar irradiance in natural waters. Appl. Opt., in press.

Kondratyev, K. Ya. 1969. <u>Radiation in the Atmosphere</u>. Academic Press, New York. 912 pp.

Madronich, S. 1987. Photodissociation in the atmosphere. I. Actinic flux and the effects of ground reflections and clouds. J. Geophys. Res. 92:9740-9752.

Prieur, L. and Sathyendranath, S. 1981. An optical classification of coastal and oceanic waters based on the specific spectral absorption curves of phytoplankton pigments, dissolved organic matter and other particulate materials. Limnol. Oceanogr. 26(4):671-689.

Zepp, G. and Cline, D.M. 1977. Rates of Photolysis in Aquatic Environment. Environ. Sci. and Technol. 11(4):359-366.

FIGURE CAPTIONS

- Figure 1 Flow diagram of the methodologies employed to convert incident radiation into scalar irradiation available for photolysis.
- Figure 2 Depth dependencies of the ratio of downwelling irradiance to scalar irradiance $D(Z,\theta,R)$ for volume reflectance $R(0^\circ) = 0.08$.
- Figure 3 $\sum_{Z} D(\theta,R)$ as a function of $R(0^{\circ})$ for five distinct Z configurations of incident radiation distributions.
- Figure 4 Relationships between the downwelling irradiance just above the air/water interface (E_d^+) and local time for the equinoxes and solstices.
- Figure 5 $\sum_{n \in Z} \sum_{n \in R} \sum_{n \in R} \sum_{n \in R} \sum_{n \in R} \sum_{n \in Z} \sum_{n \in R} \sum_{n$

Figure 6 $\sum_{\substack{\theta \in Z \\ \text{solstices}}} \sum_{\substack{D^+(R) \\ \theta \neq Z \\ \text{solstices}}} \sum_{\substack{\text{for direct} \\ \text{and diffuse} \\ \text{incident} \\ \text{radiation} \\ \text{distributions.} \\ \text{These are the multiplicative factors to} \\ \text{convert above surface daily irradiation into subsurface} \\ \text{daily scalar irradiation.} \\ \end{array}$

c1	,c2	¢3
6.076	-13.32	35.11
5.927	-14.67	43.79
6.244	-25.82	86.12
6.237	-28.28	79.76
5.866	-27.73	76.51
6.244	-25.82	86.12
	c ₁ 6.076 5.927 6.244 6.237 5.866 6.244	c1 c2 6.076 -13.32 5.927 -14.67 6.244 -25.82 6.237 -28.28 5.866 -27.73 6.244 -25.82

Table 1. Constants for the Polynomial Expansion of Equation (2)



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Figure 2



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Figure 3









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