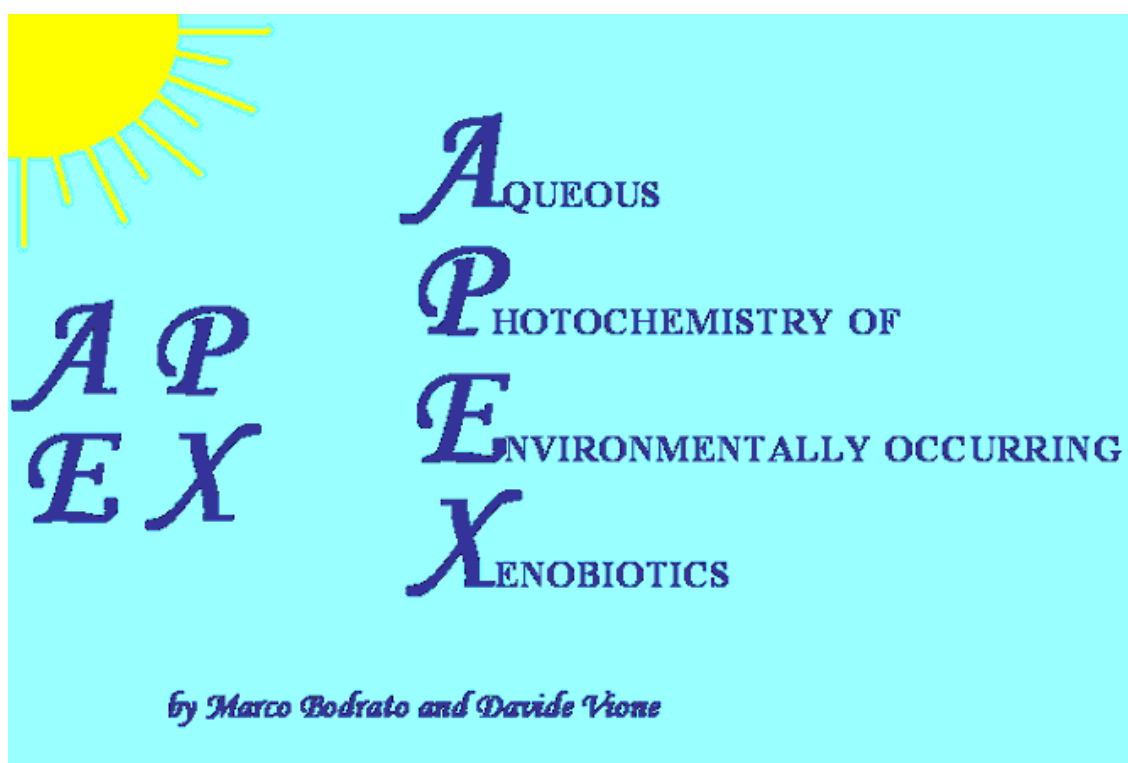


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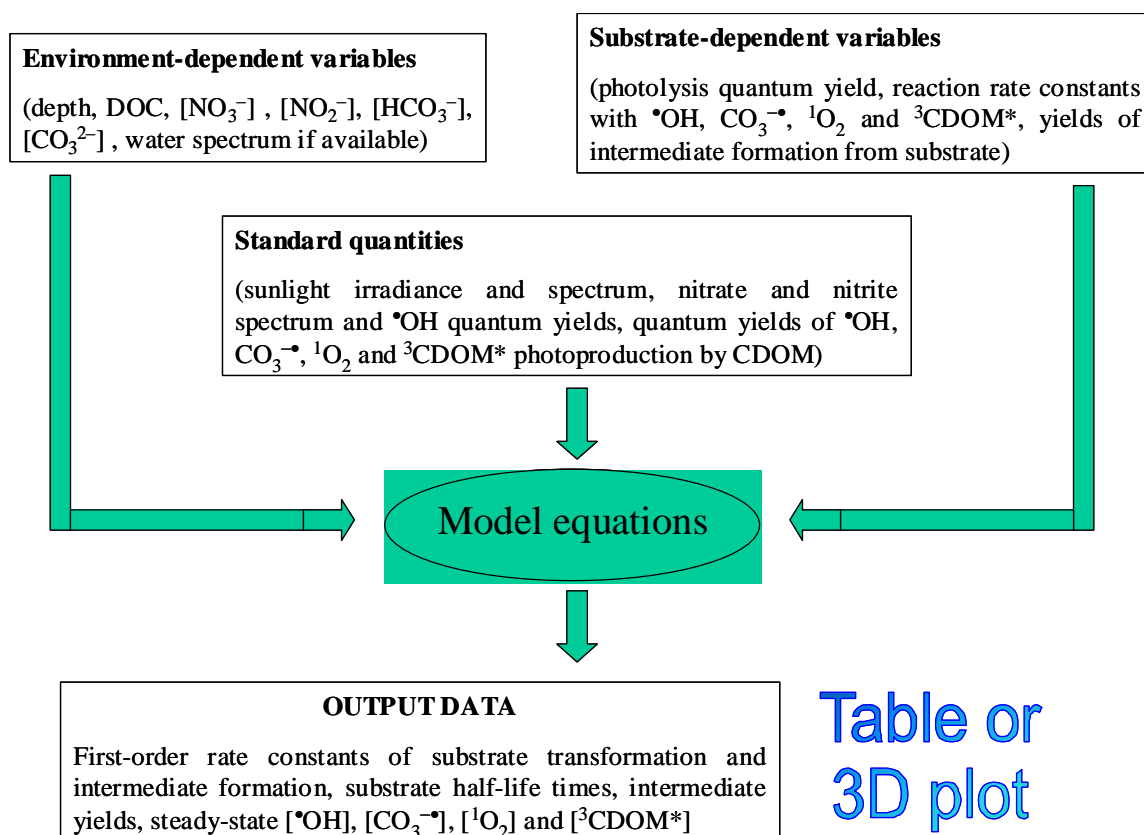
1. Introduction

Apex (Aqueous photochemistry of environmentally-occurring xenobiotics) is a code to predict the fate of aqueous pollutants, as a function of environmental features and of intrinsic substrate reactivity toward the main photochemical processes that take place in surface waters (direct photolysis and reaction with $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$).

Environmental features that can be defined as input data are water depth and chemical composition. In particular, chemical parameters that significantly affect photochemistry are nitrate, nitrite, carbonate, bicarbonate and dissolved organic carbon (DOC, sometimes also named NPOC: non-purgeable organic carbon).

Substrate-dependent features are connected with photochemical reactivity (photolysis quantum yield and reaction rate constants) and to intermediate formation yields *via* the relevant processes.

The fate of xenobiotics is described by output variables such as first-order transformation rate constants, half-life times and rate constants of intermediate formation. The model also returns steady-state $[\bullet\text{OH}]$, $[\text{CO}_3^{\bullet-}]$, $[^1\text{O}_2]$ and $[^3\text{CDOM}^*]$. An overall scheme of Apex is provided below.



The model equations are described in the following section.

2. The photochemical model for surface waters

The model describes the transformation kinetics of a substrate, a generic pollutant P, as a function of water chemistry and substrate reactivity, *via* the main photochemical reaction pathways (direct photolysis and reaction with $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$). It also calculates the steady-state concentrations of photogenerated transients in a cylindrical volume of 1 cm^2 surface area and depth d . The model may use actual data of water absorption spectrum or, in their absence, it can approximate the spectrum from the dissolved organic carbon (DOC) values. The different aspects of the model are now described in greater detail.

2.1. Surface-water absorption spectrum

It is possible to find a reasonable correlation between the absorption spectrum of surface waters and their content of dissolved organic matter, expressed as NPOC (Non-Purgeable Organic Carbon). The following equation holds for the water spectrum, referred to an optical path length of 1 cm :¹

$$A_1(\lambda) = (0.45 \pm 0.04) \cdot \text{NPOC} \cdot e^{-(0.015 \pm 0.002)\lambda} \quad (1)$$

As an obvious alternative, $A_1(\lambda)$ can be spectrophotometrically determined on a real water sample.

2.2. Reaction with $\bullet\text{OH}$ ¹

In natural surface waters under sunlight illumination, the main $\bullet\text{OH}$ sources are (in order of average importance) Chromophoric Dissolved Organic Matter (CDOM), nitrite, and nitrate. All these species produce $\bullet\text{OH}$ upon absorption of sunlight. The calculation of the photon fluxes absorbed by CDOM, nitrate and nitrite requires to take into account the mutual competition for sunlight irradiance. Actually, CDOM is the main radiation absorber in the 300-500 nm region where also nitrite and nitrate absorb radiation. At a given wavelength λ , the ratio of the photon flux densities absorbed by two different species is equal to the ratio of the respective absorbances. The same is also true for the ratio of the photon flux density absorbed by species to the total photon flux density absorbed by the solution, $p_a^{\text{tot}}(\lambda)$.² Accordingly, the following equations hold for the different $\bullet\text{OH}$ sources (note that $A_1(\lambda)$ is the specific absorbance of the surface water layer over a 1 cm optical path length, in units of cm^{-1} ; d is the water column depth in m; $A_{\text{tot}}(\lambda)$ the total absorbance of the water column, and $p^\circ(\lambda)$ the spectrum of sunlight, expressed as incident photon flux density):

¹ D. Vione, R. Das, F. Rubertelli, V. Maurino, C. Minero, S. Barbati, S. Chiron, Modelling the occurrence and reactivity of hydroxyl radicals in surface waters: Implications for the fate of selected pesticides. Intern. J. Environ. Anal. Chem. 90 (2010) 258-273.

² S. E. Braslavsky, Glossary of terms used in photochemistry, 3rd edition. Pure Appl. Chem. 79 (2007) 293-465.

$$A_{tot}(\lambda) = 100 A_1(\lambda) \cdot d \quad (2)$$

$$A_{NO3-}(\lambda) = 100 \varepsilon_{NO3-}(\lambda) \cdot d \cdot [NO_3^-] \quad (3)$$

$$A_{NO2-}(\lambda) = 100 \varepsilon_{NO2-}(\lambda) \cdot d \cdot [NO_2^-] \quad (4)$$

$$A_{CDOM}(\lambda) = A_{tot}(\lambda) - A_{NO3-}(\lambda) - A_{NO2-}(\lambda) \approx A_{tot}(\lambda) \quad (5)$$

$$p_a^{tot}(\lambda) = p^o(\lambda) \cdot (1 - 10^{-A_{tot}(\lambda)}) \quad (6)$$

$$p_a^{CDOM}(\lambda) = p_a^{tot}(\lambda) \cdot A_{CDOM}(\lambda) \cdot [A_{tot}(\lambda)]^{-1} \approx p_a^{tot}(\lambda) \quad (7)$$

$$p_a^{NO2-}(\lambda) = p_a^{tot}(\lambda) \cdot A_{NO2-}(\lambda) \cdot [A_{tot}(\lambda)]^{-1} \quad (8)$$

$$p_a^{NO3-}(\lambda) = p_a^{tot}(\lambda) \cdot A_{NO3-}(\lambda) \cdot [A_{tot}(\lambda)]^{-1} \quad (9)$$

An important issue is that $p^o(\lambda)$ is usually reported in units of Einstein $\text{cm}^{-2} \text{s}^{-1} \text{nm}^{-1}$ (see for instance Figure 1), thus the absorbed photon flux densities are expressed in the same units. To express the formation rates of $\bullet\text{OH}$ in M s^{-1} , the absorbed photon fluxes P_a^i should be expressed in Einstein $\text{L}^{-1} \text{s}^{-1}$. Integration of $p_a^i(\lambda)$ over wavelength would give units of Einstein $\text{cm}^{-2} \text{s}^{-1}$ that represent the moles of photons absorbed per unit surface area and unit time.

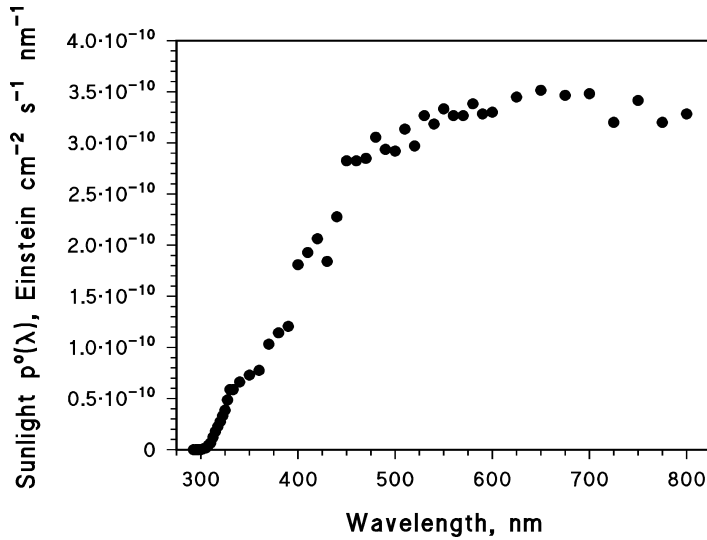


Figure 1. Sunlight spectral photon flux density at the water surface per unit area. The corresponding UV irradiance is 22 W m^{-2} .³

Assuming a cylindrical volume of unit surface area (1 cm^2) and depth d (expressed in m), the absorbed photon fluxes in Einstein $\text{L}^{-1} \text{s}^{-1}$ units would be expressed as follows (note that $1 \text{ L} = 10^3 \text{ cm}^3$ and $1 \text{ m} = 10^2 \text{ cm}$):

$$P_a^{CDOM} = 10 d^{-1} \int_{\lambda} p_a^{CDOM}(\lambda) d\lambda \quad (10)$$

$$P_a^{NO2-} = 10 d^{-1} \int_{\lambda} p_a^{NO2-}(\lambda) d\lambda \quad (11)$$

³ R. Frank, W. Klöpffer, Spectral solar photo irradiance in Central Europe and the adjacent north Sea, Chemosphere 17 (1988) 985-994.

$$P_a^{NO3-} = 10 d^{-1} \int_{\lambda} p_a^{NO3-}(\lambda) d\lambda \quad (12)$$

Various studies have yielded useful correlation between the formation rate of $\bullet\text{OH}$ by the photoactive species and the respective absorbed photon fluxes of sunlight. In particular, it has been found that:^{1,4,5}

$$R_{\bullet\text{OH}}^{CDOM} = (3.0 \pm 0.4) \cdot 10^{-5} \cdot P_a^{CDOM} \quad (13)$$

$$R_{\bullet\text{OH}}^{NO2-} = \int_{\lambda} \Phi_{\bullet\text{OH}}^{NO2-}(\lambda) p_a^{NO2-}(\lambda) d\lambda \quad (14)$$

$$R_{\bullet\text{OH}}^{NO3-} = (4.3 \pm 0.2) \cdot 10^{-2} \cdot \frac{[IC] + 0.0075}{2.25 [IC] + 0.0075} \cdot P_a^{NO3-} \quad (15)$$

where $[IC] = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ is the total amount of inorganic carbon. The wavelength-dependent data of $\Phi_{\bullet\text{OH}}^{NO2-}(\lambda)$ are reported in Table 1.⁵

Table 1. Values of the quantum yield of $\bullet\text{OH}$ photoproduction by nitrite, for different wavelengths of environmental significance.

λ , nm	$\Phi_{\bullet\text{OH}}^{NO2-}(\lambda)$	λ , nm	$\Phi_{\bullet\text{OH}}^{NO2-}(\lambda)$	λ , nm	$\Phi_{\bullet\text{OH}}^{NO2-}(\lambda)$
292.5	0.0680	315.0	0.061	350	0.025
295.0	0.0680	317.5	0.058	360	0.025
297.5	0.0680	320.0	0.054	370	0.025
300.0	0.0678	322.5	0.051	380	0.025
302.5	0.0674	325.0	0.047	390	0.025
305.0	0.0668	327.5	0.043	400	0.025
307.5	0.066	330.0	0.038	410	0.025
310.0	0.065	333.3	0.031	420	0.025
312.5	0.063	340.0	0.026	430	0.025

At the present state of knowledge it is reasonable to hypothesise that CDOM, nitrite and nitrate generate $\bullet\text{OH}$ independently, with no mutual interactions. Therefore, the total formation rate of $\bullet\text{OH}$ ($R_{\bullet\text{OH}}^{tot}$) is the sum of the contributions of the three species:

$$R_{\bullet\text{OH}}^{tot} = R_{\bullet\text{OH}}^{CDOM} + R_{\bullet\text{OH}}^{NO2-} + R_{\bullet\text{OH}}^{NO3-} \quad (16)$$

Accordingly, having as input data d , $A_I(\lambda)$, $[\text{NO}_3^-]$, $[\text{NO}_2^-]$ and $p^\circ(\lambda)$ (the latter referred to a 22 W m⁻² sunlight UV irradiance, see Figure 1), it is possible to model the expected $R_{\bullet\text{OH}}^{tot}$ of the sample. The photogenerated $\bullet\text{OH}$ radicals could react either with the pollutant P or with the natural

⁴ D. Vione, S. Khanra, S. Cucu Man, P. R. Maddigapu, R. Das, C. Arsene, R. I. Olariu, V. Maurino, C. Minero, Inhibition vs. enhancement of the nitrate-induced phototransformation of organic substrates by the $\bullet\text{OH}$ scavengers bicarbonate and carbonate. Wat. Res. 43 (2009) 4718-4728.

⁵ J. Mack, J.R. Bolton, Photochemistry of nitrite and nitrate in aqueous solution: a review, J. Photochem. Photobiol. A: Chem. 128 (1999) 1-13.

scavengers present in surface water (mainly organic matter, bicarbonate, carbonate and nitrite). The natural scavengers have the following $\bullet\text{OH}$ scavenging rate constant:

$\sum_i k_{Si} [S_i] = 5 \times 10^4 \text{ NPOC} + 8.5 \times 10^6 [\text{HCO}_3^-] + 3.9 \times 10^8 [\text{CO}_3^{2-}] + 1.0 \times 10^{10} [\text{NO}_2^-]$ (units of s^{-1} ; NPOC = non-purgeable organic carbon is a measure of DOC, expressed in mg C L^{-1} , and the other concentration values are in molarity). Accordingly, the reaction rate between P and $\bullet\text{OH}$ can be expressed as follows:

$$R_P^{\bullet\text{OH}} = R_{\bullet\text{OH}}^{\text{tot}} \frac{k_{P,\bullet\text{OH}} [P]}{k_{P,\bullet\text{OH}} [P] + \sum_i k_{Si} [S_i]} \quad (17)$$

where $k_{P,\bullet\text{OH}}$ is the second-order reaction rate constant between P and $\bullet\text{OH}$, and [P] is a molar concentration. Note that, in the vast majority of environmental cases it would be $k_{P,\bullet\text{OH}} [P] \ll \sum_i k_{Si} [S_i]$, thus the $k_{P,\bullet\text{OH}} [P]$ term can be neglected at the denominator of equation (17). The pseudo-first order degradation rate constant of P is $k_P = R_{\bullet\text{OH}}^{\text{tot}} [P]^{-1}$, and the half-life time is $t_P = \ln 2 k_P^{-1}$. The time t_P is expressed in seconds of continuous irradiation under sunlight, at 22 W m^{-2} UV irradiance (see Figure 1 for the sunlight spectrum). It has been shown that the sunlight energy reaching the ground in a summer sunny day (SSD) such as 15 July at 45°N latitude corresponds to $10 \text{ h} = 3.6 \cdot 10^4 \text{ s}$ of continuous irradiation at 22 W m^{-2} UV irradiance.⁶ Accordingly the half-life time of P, because of reaction with $\bullet\text{OH}$, would be expressed as follows in SSD units:

$$\tau_{P,\bullet\text{OH}}^{\text{SSD}} = \frac{\ln 2 \sum_i k_{Si} [S_i]}{3.6 \cdot 10^4 R_{\bullet\text{OH}}^{\text{tot}} k_{P,\bullet\text{OH}}} = 1.9 \cdot 10^{-5} \frac{\sum_i k_{Si} [S_i]}{R_{\bullet\text{OH}}^{\text{tot}} k_{P,\bullet\text{OH}}} \quad (18)$$

Note that $1.9 \cdot 10^{-5} = \ln 2 (3.6 \cdot 10^4)^{-1}$. The steady-state $[\bullet\text{OH}]$ under 22 W m^{-2} UV irradiance would be:

$$[\bullet\text{OH}] = \frac{R_{\bullet\text{OH}}^{\text{tot}}}{\sum_i k_{Si} [S_i]} \quad (19)$$

Also note that the function **apex.m** adopts a slightly different definition of $R_{\bullet\text{OH}}^{\text{tot}}$, namely the formation rate of $\bullet\text{OH}$ inside a cylinder of volume $V = 0.1 \text{ d}$ (units of mol s^{-1} instead of $\text{mol L}^{-1} \text{ s}^{-1}$). For this reason, the term $V = 0.1 \text{ d}$ is included in equation that is equivalent to (18).

2.3. Direct photolysis^{7,8}

The calculation of the photon flux absorbed by P requires taking into account the mutual competition for sunlight irradiance between P and the other water components (mostly

⁶ C. Minero, S. Chiron, G. Falletti, V. Maurino, E. Pelizzetti, R. Ajassa, M. E. Carlotti, D. Vione, Photochemical processes involving nitrite in surface water samples. *Aquat. Sci.* 69 (2007) 71-85.

⁷ D. Vione, J. Feitosa-Felizzola, C. Minero, S. Chiron, Phototransformation of selected human-used macrolides in surface water: Kinetics, model predictions and degradation pathways. *Wat. Res.* 43 (2009) 1959-1967.

⁸ D. Vione, M. Minella, C. Minero, V. Maurino, P. Picco, A. Marchetto, G. Tartari, Photodegradation of nitrite in lake waters: role of dissolved organic matter. *Environ. Chem.* 6 (2009) 407-415.

Chromophoric Dissolved Organic Matter, CDOM, which is the main sunlight absorber in the spectral region of interest, around 300-500 nm).

Under the Lambert-Beer approximation, at a given wavelength λ , the ratio of the photon flux densities absorbed by two different species is equal to the ratio of the respective absorbances.² Accordingly, the photon flux absorbed by P in a water column of depth d (expressed in m) can be obtained as follows (note that $A_I(\lambda)$ is the specific absorbance of the surface water sample over a 1 cm optical path length, $A_{tot}(\lambda)$ the total absorbance of the water column, $p^\circ(\lambda)$ the spectrum of sunlight, referred to a UV irradiance of 22 W m^{-2} as per Figure 1, $\varepsilon_P(\lambda)$ the molar absorption coefficient of P, in units of $\text{M}^{-1} \text{ cm}^{-1}$, and $p_a^P(\lambda)$ its absorbed spectral photon flux density; it is also $p_a^P(\lambda) \ll p_a^{tot}(\lambda)$ and $A_P(\lambda) \ll A_{tot}(\lambda)$ in the very vast majority of the environmental cases):

$$A_{tot}(\lambda) = 100 A_I(\lambda) \cdot d \quad (20)$$

$$A_P(\lambda) = 100 \varepsilon_P(\lambda) \cdot d \cdot [P] \quad (21)$$

$$p_a^{tot}(\lambda) = p^\circ(\lambda) \cdot (1 - 10^{-A_{tot}(\lambda)}) \quad (22)$$

$$p_a^P(\lambda) = p_a^{tot}(\lambda) \cdot A_P(\lambda) \cdot [A_{tot}(\lambda)]^{-1} \quad (23)$$

To express the rate of P photolysis in M s^{-1} , the absorbed photon flux P_a^P should be expressed in $\text{Einstein L}^{-1} \text{ s}^{-1}$. Integration of $p_a^P(\lambda)$ over wavelength gives units of $\text{Einstein cm}^{-2} \text{ s}^{-1}$ that represent the moles of photons absorbed per unit surface area and unit time. Assuming a cylindrical volume of unit surface area (1 cm^2) and depth d (expressed in m), the absorbed photon flux in $\text{Einstein L}^{-1} \text{ s}^{-1}$ units would be expressed as follows (note that $1 \text{ L} = 10^3 \text{ cm}^3$ and $1 \text{ m} = 10^2 \text{ cm}$):

$$P_a^P = 10 d^{-1} \int_{\lambda} p_a^P(\lambda) d\lambda \quad (24)$$

The rate of photolysis of P, expressed in M s^{-1} , is (note that $1 \text{ L} = 10^3 \text{ cm}^3$ and $1 \text{ m} = 10^2 \text{ cm}$):

$$\text{Rate}_P = 10 d^{-1} \int_{\lambda} \Phi_P(\lambda) p_a^P(\lambda) d\lambda \quad (25)$$

where $\Phi_P(\lambda)$ is the photolysis quantum yield of P in the relevant wavelength interval, and d is expressed in cm (also note that $1 \text{ L} = 10^3 \text{ cm}^3$). If only a single average value for Φ_P is known, it can be brought out of the integral as a constant. The pseudo-first order degradation rate constant of P is $k_P = \text{Rate}_P [P]^{-1}$, which corresponds to a half-life time $t_P = \ln 2 (k_P)^{-1}$. The time t_P is expressed in seconds of continuous irradiation under sunlight, at 22 W m^{-2} UV irradiance. The sunlight energy reaching the ground in a summer sunny day (SSD) such as 15 July at 45°N latitude corresponds to $10 \text{ h} = 3.6 \cdot 10^4 \text{ s}$ continuous irradiation at 22 W m^{-2} UV irradiance.⁶ Accordingly, the half-life time expressed in SSD units would be given by (note that $V = 0.1 d$):

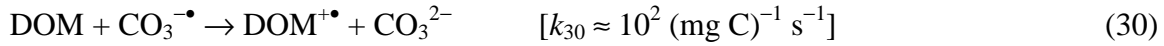
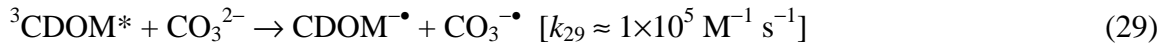
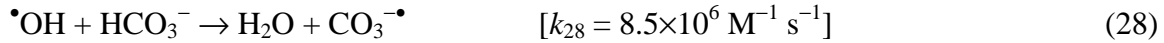
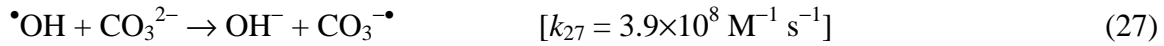
$$\begin{aligned} \tau_P^{SSD} &= (3.6 \cdot 10^4)^{-1} \ln 2 (k_P)^{-1} = 1.9 \cdot 10^{-5} [P] (\text{Rate}_P)^{-1} = \\ &= 1.9 \cdot 10^{-5} [P] V \left(\int_{\lambda} \Phi_P(\lambda) p_a^P(\lambda) d\lambda \right)^{-1} = \end{aligned}$$

$$= \frac{1.9 \cdot 10^{-5} [P] V \left(\int_{\lambda} \Phi_p(\lambda) \cdot p_a^{tot}(\lambda) \cdot A_p(\lambda) \cdot [A_{tot}(\lambda)]^{-1} d\lambda \right)^{-1}}{1.9 \cdot 10^{-5} V [P]} = \frac{\int_{\lambda} \Phi_p(\lambda) p^o(\lambda) (1 - 10^{-100 A_1(\lambda) d}) \frac{\epsilon_p(\lambda)}{A_1(\lambda)} d\lambda}{1.9 \cdot 10^{-5} V [P]} \quad (26)$$

Note that $1.9 \cdot 10^{-5} = (\ln 2) (3.6 \cdot 10^4)^{-1}$.

2.4. Reaction with $\text{CO}_3^{\bullet-}$ ⁹

The radical $\text{CO}_3^{\bullet-}$ can be produced upon oxidation of carbonate and bicarbonate by $\bullet\text{OH}$, upon carbonate oxidation by $^3\text{CDOM}^*$, and possibly also from irradiated Fe(III) oxide colloids and carbonate. However, as far as the latter process is concerned, there is still insufficient knowledge about the Fe speciation in surface waters to enable a proper modelling. The main sink of the carbonate radical in surface waters is the reaction with DOM, which is considerably slower than that between DOM and $\bullet\text{OH}$.



The formation rate of $\text{CO}_3^{\bullet-}$ in reactions (27, 28) is given by the formation rate of $\bullet\text{OH}$ times the fraction of $\bullet\text{OH}$ that reacts with carbonate and bicarbonate, as follows:

$$R_{\text{CO}_3^{\bullet-}}^{\bullet\text{OH}} = R_{\bullet\text{OH}}^{\text{tot}} \cdot \frac{8.5 \cdot 10^6 \cdot [\text{HCO}_3^-] + 3.9 \cdot 10^8 \cdot [\text{CO}_3^{2-}]}{5 \cdot 10^4 \cdot \text{NPOC} + 1.0 \cdot 10^{10} \cdot [\text{NO}_2^-] + 8.5 \cdot 10^6 \cdot [\text{HCO}_3^-] + 3.9 \cdot 10^8 \cdot [\text{CO}_3^{2-}]} \quad (31)$$

The formation of $\text{CO}_3^{\bullet-}$ in reaction (29) is given by:

$$R_{\text{CO}_3^{\bullet-}}^{\text{CDOM}} = 6.5 \cdot 10^{-3} \cdot [\text{CO}_3^{2-}] \cdot P_a^{\text{CDOM}} \quad (32)$$

The total formation rate of $\text{CO}_3^{\bullet-}$ is $R_{\text{CO}_3^{\bullet-}}^{\text{tot}} = R_{\text{CO}_3^{\bullet-}}^{\bullet\text{OH}} + R_{\text{CO}_3^{\bullet-}}^{\text{CDOM}}$. The transformation rate of P by $\text{CO}_3^{\bullet-}$ is given by the fraction of $\text{CO}_3^{\bullet-}$ that reacts with P, in competition with reaction (30) between $\text{CO}_3^{\bullet-}$ and DOM:

$$R_{\text{P,CO}_3^{\bullet-}} = \frac{R_{\text{CO}_3^{\bullet-}}^{\text{tot}} \cdot k_{\text{P,CO}_3^{\bullet-}} \cdot [\text{P}]}{k_{30} \cdot \text{NPOC} + k_{\text{P,CO}_3^{\bullet-}} \cdot [\text{P}]} \quad (33)$$

⁹ D. Vione, V. Maurino, C. Minero, M. E. Carloti, S. Chiron, S. Barbati, Modelling the occurrence and reactivity of the carbonate radical in surface freshwater. C. R. Chimie 12 (2009) 865-871.

where $k_{P,CO_3^{\bullet-}}$ is the second-order reaction rate constant between P and $CO_3^{\bullet-}$. In the very vast majority of the environmental cases it is $k_{P,CO_3^{\bullet-}} [P] \ll k_{30} \text{ NPOC}$.

In a pseudo-first order approximation, the rate constant of P transformation is $k_P = R_{P,CO_3^{\bullet-}} [P]^{-1}$ and the half-life time is $t_P = \ln 2 k_P^{-1}$. Considering the usual conversion (≈ 10 h) between a constant 22 W m^{-2} sunlight UV irradiance and a SSD unit, the following expression for $\tau_{NCP,CO_3^{\bullet-}}^{SSD}$ is obtained:

$$\tau_{P,CO_3^{\bullet-}}^{SSD} = 1.9 \cdot 10^{-5} \cdot \left(\frac{k_{30} \cdot \text{NPOC}}{R_{CO_3^{\bullet-}}^{\text{tot}} \cdot k_{P,CO_3^{\bullet-}}} \right) \quad (34)$$

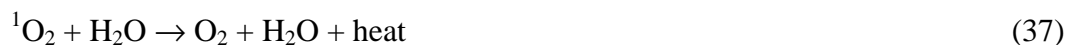
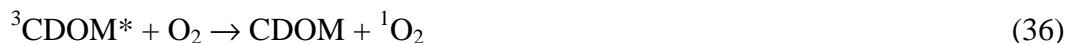
Note that $1.9 \cdot 10^{-5} = \ln 2 (3.6 \cdot 10^4)^{-1}$. The steady-state $[CO_3^{\bullet-}]$ under 22 W m^{-2} UV irradiance would be:

$$[CO_3^{\bullet-}] = \frac{R_{CO_3^{\bullet-}}^{\text{tot}}}{k_{30} \cdot \text{NPOC}} \quad (35)$$

Also note that the function **apex.m** adopts a slightly different definition of $R_{CO_3^{\bullet-}}^{\text{tot}}$, namely the formation rate of $CO_3^{\bullet-}$ inside a cylinder of volume $V = 0.1 \text{ d}$ (units of mol s^{-1} instead of $\text{mol L}^{-1} \text{ s}^{-1}$). For this reason, the term $V = 0.1 \text{ d}$ is included in the equation that is equivalent to (34) ($1.9 \cdot 10^{-4} = 1.9 \cdot 10^{-5} k_{30} 0.1$).

2.5. Reaction with 1O_2 ¹⁰

The formation of singlet oxygen in surface waters arises from energy transfer between ground-state molecular oxygen and the excited triplet states of CDOM ($^3\text{CDOM}^*$). Accordingly, irradiated CDOM is practically the only source of 1O_2 in aquatic systems. In contrast, the main 1O_2 sink is the energy loss to ground-state O_2 by collision with water molecules, with a pseudo-first order rate constant $k_{^1O_2} = 2.5 \times 10^5 \text{ s}^{-1}$. Dissolved species, including dissolved organic matter that is certainly able to react with 1O_2 would play a minor role as sinks of 1O_2 in aquatic systems. The main processes involving 1O_2 and P in surface waters would be the following:



¹⁰ D. Vione, R. Das, F. Rubertelli, V. Maurino, C. Minero, Modeling of indirect phototransformation processes in surface waters. In: Ideas in Chemistry and molecular Sciences: Advances in Synthetic Chemistry, Pignataro, B., ed., Wiley-VCH, Weinheim, Germany, 2010, pp. 203-234.

In the Rhône delta waters it has been found that the formation rate of $^1\text{O}_2$ by CDOM is $R_{^1\text{O}_2}^{\text{CDOM}} = 1.25 \cdot 10^{-3} P_a^{\text{CDOM}}$.¹¹ Considering the competition between the deactivation of $^1\text{O}_2$ by collision with the solvent (reaction 37) and reaction (38) with P, one gets the following expression for the degradation rate of P by $^1\text{O}_2$ (note that $k_{P,^1\text{O}_2} \cdot [P] \ll k_{^1\text{O}_2}$):

$$R_{P,^1\text{O}_2} = R_{^1\text{O}_2}^{\text{CDOM}} \cdot \frac{k_{P,^1\text{O}_2} \cdot [P]}{k_{^1\text{O}_2}} \quad (39)$$

In a pseudo-first order approximation, the rate constant of P transformation is $k_P = R_{P,^1\text{O}_2} [P]^{-1}$ and the half-life time is $t_P = \ln 2 \cdot k_P^{-1}$. Considering the usual conversion (≈ 10 h) between a constant 22 W m^{-2} sunlight UV irradiance and a SSD unit, the following expression for $\tau_{P,^1\text{O}_2}^{\text{SSD}}$ is obtained (remembering that $R_{^1\text{O}_2}^{\text{CDOM}} = 1.25 \cdot 10^{-3} P_a^{\text{CDOM}}$ and that $P_a^{\text{CDOM}} = 10^3 d^{-1} \int_{\lambda} p_a^{\text{CDOM}}(\lambda) d\lambda$):

$$\tau_{P,^1\text{O}_2}^{\text{SSD}} = \frac{4.81}{R_{^1\text{O}_2}^{\text{CDOM}} k_{P,^1\text{O}_2}} = \frac{3.85 \cdot d}{k_{P,^1\text{O}_2} \cdot \int_{\lambda} p_a^{\text{CDOM}}(\lambda) d\lambda} \quad (40)$$

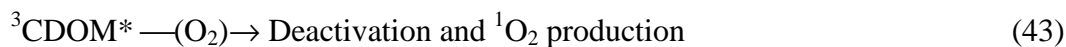
Note that $3.85 = (\ln 2) k_{^1\text{O}_2} (1.25 \cdot 10^{-3} \cdot 3.60 \cdot 10^4 \cdot 10^3)^{-1}$. The steady-state $[^1\text{O}_2]$ under 22 W m^{-2} UV irradiance would be:

$$[^1\text{O}_2] = \frac{R_{^1\text{O}_2}^{\text{CDOM}}}{k_{^1\text{O}_2}} \quad (41)$$

Also note that the function **apex.m** adopts a slightly different definition of $R_{^1\text{O}_2}^{\text{CDOM}}$, namely the formation rate of $^1\text{O}_2$ inside a cylinder of volume $V = 0.1 d$ (units of mol s^{-1} instead of $\text{mol L}^{-1} \text{ s}^{-1}$). For this reason, the term $V = 0.1 d$ is included in the equation that is equivalent to (40).

2.6. Reaction with $^3\text{CDOM}^*$ ¹⁰

The formation of excited triplet states of CDOM ($^3\text{CDOM}^*$) in surface waters is a direct consequence of radiation absorption by CDOM. In aerated solution, $^3\text{CDOM}^*$ could undergo thermal deactivation or reaction with O_2 , and a pseudo-first order quenching rate constant $k_{^3\text{CDOM}^*} \approx 5 \cdot 10^5 \text{ s}^{-1}$ has been observed. The quenching of $^3\text{CDOM}^*$ would be in competition with the reaction between $^3\text{CDOM}^*$ and P:



¹¹ F. Al-Housari, D. Vione, S. Chiron, S. Barbati, Reactive photoinduced species in estuarine waters. Characterization of hydroxyl radical, singlet oxygen and dissolved organic matter triplet state in natural oxidation processes. Photochem. Photobiol. Sci. 9 (2010) 78-86.



In the Rhône delta waters it has been found that the formation rate of ${}^3\text{CDOM}^*$ is $R_{{}^3\text{CDOM}^*} = 1.28 \cdot 10^{-3} P_a^{\text{CDOM}}$.¹¹ Considering the competition between reaction (44) with P and other processes (reaction 43), the following expression for the degradation rate of P by ${}^3\text{CDOM}^*$ is obtained (note that $k_{P,{}^3\text{CDOM}^*} \cdot [P] \ll k_{{}^3\text{CDOM}^*}$, where $k_{P,{}^3\text{CDOM}^*}$ is the second-order reaction rate constant between P and ${}^3\text{CDOM}^*$):

$$R_P^{{}^3\text{CDOM}^*} = R_{{}^3\text{CDOM}^*} \cdot \frac{k_{P,{}^3\text{CDOM}^*} \cdot [P]}{k_{{}^3\text{CDOM}^*}} \quad (45)$$

In a pseudo-first order approximation, the rate constant for P transformation is $k_P = R_P^{{}^3\text{CDOM}^*} [P]^{-1}$ and the half-life time is $t_P = \ln 2 \cdot k_P^{-1}$. Considering the usual conversion (≈ 10 h) between a constant 22 W m^{-2} sunlight UV irradiance and a SSD unit, one gets the following expression for $\tau_{P,{}^3\text{CDOM}^*}^{\text{SSD}}$ (remembering that $P_a^{\text{CDOM}} = 10^3 \text{ d}^{-1} \int_{\lambda} p_a^{\text{CDOM}}(\lambda) d\lambda$):

$$\tau_{P,{}^3\text{CDOM}^*}^{\text{SSD}} = \frac{7.52 \cdot d}{k_{P,{}^3\text{CDOM}^*} \cdot \int_{\lambda} p_a^{\text{CDOM}}(\lambda) d\lambda} \quad (46)$$

Note that $7.52 = (\ln 2) \cdot k_{{}^3\text{CDOM}^*} (1.28 \cdot 10^{-3} \cdot 3.60 \cdot 10^4 \cdot 10^3)^{-1}$. The steady-state $[{}^3\text{CDOM}^*]$ under 22 W m^{-2} UV irradiance would be:

$$[{}^3\text{CDOM}^*] = \frac{R_{{}^3\text{CDOM}^*}}{k_{{}^3\text{CDOM}^*}} \quad (47)$$

Also note that the function *apex.m* adopts a slightly different definition of $R_{{}^3\text{CDOM}^*}$, namely the formation rate of ${}^3\text{CDOM}^*$ inside a cylinder of volume $V = 0.1 \text{ d}$ (units of mol s^{-1} instead of $\text{mol L}^{-1} \text{ s}^{-1}$). For this reason, the term $V = 0.1 \text{ d}$ is included in the equation that is equivalent to (46).

2.7. Formation of intermediates¹²

In the photochemical process *ph* (direct photolysis or reaction with $\bullet\text{OH}$, ${}^1\text{O}_2$, $\text{CO}_3^{\bullet-}$, ${}^3\text{CDOM}^*$), the pollutant P could produce the intermediate I with yield y_I^{ph} , experimentally determined as the ratio between the initial formation rate of I and the initial transformation rate of P. The pseudo-first order rate constant of I formation in the process *ph* is $(k_I^{ph})' = y_I^{ph} k_P^{ph}$, where k_P^{ph} is the (model-derived)

¹² E. De Laurentiis, S. Chiron, S. Kouras-Hadef, C. Richard, M. Minella, V. Maurino, C. Minero, D. Vione, Photochemical fate of carbamazepine in surface freshwaters: Laboratory measures and modelling. Environ. Sci. Technol. 46 (2012) 8164-8173.

first-order transformation rate constant of P in the process *ph*. The production of I from P often takes place *via* more than one process. Therefore, the overall rate constant of I formation is:

$$(k_I)' = \sum_{ph} (k_I^{ph})' = \sum_{ph} (y_I^{ph} k_I^{ph}) \quad (48)$$

One can also obtain the overall yield of I formation from P (y_I), as:

$$y_I = (k_I)'(k_P)^{-1} = \frac{\sum_{ph} (y_I^{ph} k_I^{ph})}{\sum_{ph} k_P^{ph}} \quad (49)$$

2.8. The meaning of water depth in the model

An important issue is that the model was not designed to make depth profiles of the transformation kinetics or of the concentration of reactive transients. Therefore, when setting depth as a variable one actually compares different water bodies, each with its own depth value. This means that for, *e.g.*, 1 m depth the model returns the average [\bullet OH] (or the steady-state concentration of other species) in the first 1 m of the water column. It should be underlined that it is the average concentration in the first 1 m of the column and not the point concentration at 1 m. One can also obtain the transformation kinetics of dissolved species in the hypothesis of thorough mixing in the water column, because the model applies to well-mixed shallow waters or to the top mixing layer of stratified water bodies. A key issue is that, if one wants to determine the photochemical reaction kinetics due to *e.g.* reaction with \bullet OH in the first 1 m of the water column, the needed value is the average [\bullet OH] value (as determined by the model) and not the point [\bullet OH] at 1 m.

2.9. Main approximations of the model

Surface waters represent an extremely complex and varied series of environments and the present attempt to describe their photochemical behaviour had to include a number of assumptions and approximations. The main ones are listed below.

- The model considers well-mixed water. Therefore, it applies to shallow water environments and to the well-mixed epilimnion of stratified ones.
- The Lambert-Beer approximation does not take radiation scattering into account. Therefore, the model applies to clear waters rather than to highly turbid ones.
- The data on which the modelling of surface-water absorption spectrum is based (equation 1) were obtained for lake water in NW Italy. There is evidence that applicability is much wider,

but more accurate results for a particular environment can be obtained if the actual water spectrum is available.

- The quantum yields for the formation of $\bullet\text{OH}$ by CDOM are average values for NW Italian lakes. The corresponding values for $^1\text{O}_2$ and $^3\text{CDOM}^*$ have been obtained in the Rhône delta (S. France), and the value of $\text{CO}_3^-\bullet$ formation from $^3\text{CDOM}^*$ is from Lake Greifensee (Switzerland). In different environments, different values may be found. The best scenario is obviously attained when one has data that have been measured in the water environment under study.
- The scavenging rate constants of $\bullet\text{OH}$ and $\text{CO}_3^-\bullet$ by DOM are average values from the literature. The same consideration as above also applies here.

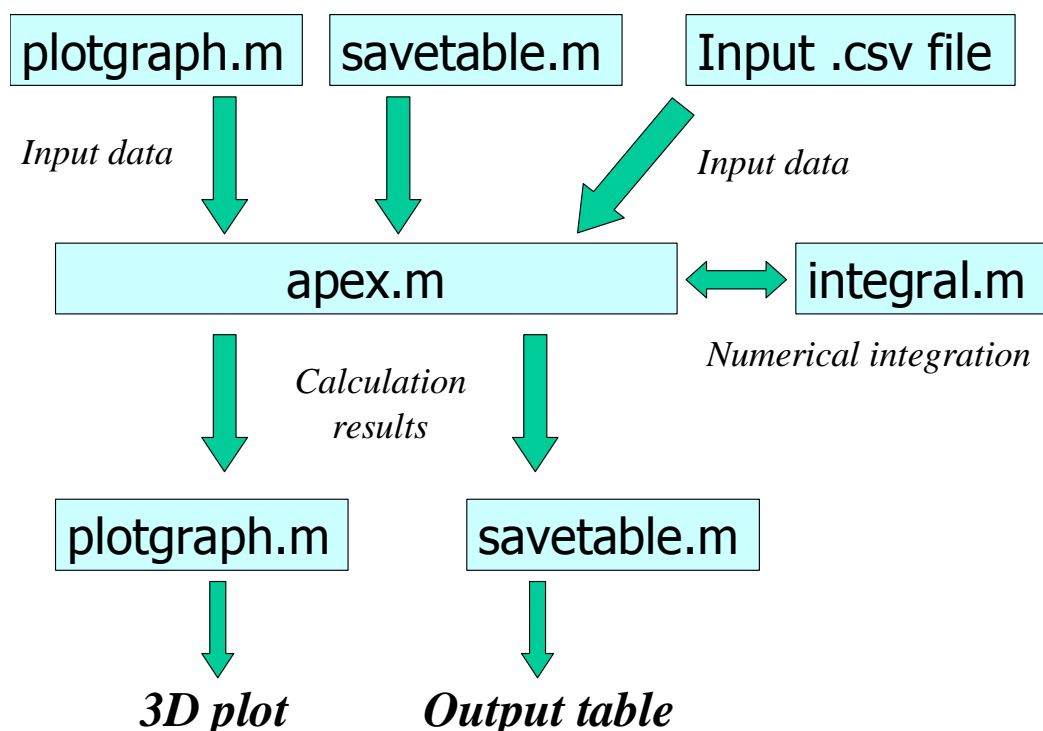
Despite its approximations, the model could be quite useful for laboratory scientists who measure the photochemical degradation of pollutants and would like to have an assessment of the environmental significance of their findings. The possibility to model the water absorption spectrum, instead of having to use experimentally measured data could be particularly useful, if one wants to see the significance of different photochemical pathways under variable conditions.

In contrast, if one wants to describe a particular environment, the best way to increase the accuracy of the results is to use measured values from that environment. Such values are water absorption spectrum, formation quantum yields of $\bullet\text{OH}$, $^1\text{O}_2$, $\text{CO}_3^-\bullet$ and $^3\text{CDOM}^*$ by CDOM, and scavenging rate constants of $\bullet\text{OH}$ and $\text{CO}_3^-\bullet$ by DOM.

3. Apex

Apex is a tool to model photochemical processes in surface waters. Available for free download as a .zip file (<http://chimica.campusnet.unito.it/do/didattica.pl/Quest?corso=7a3d>), Apex is based on Octave, an Open Source and freely available mathematics software (<http://www.gnu.org/software/octave>). For using Apex, Octave should be downloaded and installed. It has been developed for Linux, but Windows versions of Octave are also available for free download (<http://sourceforge.net/projects/octave/files/Octave%20Windows%20binaries/>), as well as versions for Mac OSX ([http://wiki.octave.org/Octave for MacOS X](http://wiki.octave.org/Octave_for_MacOS_X)). After download and installation, one has to launch Octave and to run Apex within Octave. To make this easier, it is advisable to have the Apex folder under the main root (e.g. as C:\Apex). An easy way to do so is to save the downloaded Apex.zip file under C:\, and then use the “Extract to here” option of WinZip (Apex.zip already contains the files in the \Apex folder).

Apex is based on a series of functions: `plotgraph.m` (data input and 3D graph plot), `savetable.m` (data input and generation of a table with numerical output data), `apex.m` (model calculations), `integral.m` (numerical integration). In addition, `apexvec.m` is used to produce the output format by both Plotgraph and Savetable. Finally, part of the input data are contained in a .csv file. The scheme below gives insight into the flow of information within Apex.



All the functions (`plotgraph.m`, `savetable.m`, `apex.m`, `integral.m` and `apexvec.m`) can be read (and modified) with a normal text editor (such as Windows' Notepad). In theory a word processor could also be used but it is not recommended because, while saving the files, it might add additional lines. These would not be understood by Octave and would cause the generation of error messages.

The overall procedure to use Apex is reported below. The different parts will be explained in detail in the next chapters.

- 1) Create or open (to modify and/or check) the input .csv file (it contains data of the target compound such as absorption spectrum and photolysis quantum yield, as well as additional information).
- 2) Open and modify plotgraph.m and/or savetable.m, to introduce input data.
- 3) Launch Octave to create the 3D plot or the output table.

WARNING. The user needs to open the functions plotgraph.m and savetable.m to insert some of the input data. This implies a risk of accidentally causing irreversible damage to those files. For this reason, in addition to the main Apex folder, it is advisable to have a second one where to store the original Apex files after download, so that they can be quickly retrieved if needed.

NOTE: Apex has been developed in a Linux environment and it has been extensively tested with the 3.2.4 version of Octave. Some of the earlier Octave versions (*e.g.*, 2.*) might not work properly with Apex. Successful running of Apex with Octave 3.2.4 has been carried out with Windows Me, 2000, XP and 7. Other operating systems have not been tested.

4. Input file (.csv)

All the wavelength-dependent parameters are contained in a .csv file. The file contains both compound-dependent parameters, and parameters of general use. The standard adopted by default is to name the file after the compound it is referred to. The columns present in the input file will now be listed.

Column 1: Wavelength.

Column 2: $\epsilon_{NO_3^-}$. Molar absorption coefficient of nitrate, in $M^{-1} cm^{-1}$ units.

Column 3: $\epsilon_{NO_2^-}$. Molar absorption coefficient of nitrite, in $M^{-1} cm^{-1}$ units.

Column 4: $\Phi_{NO_2^- \rightarrow \bullet OH}$. Quantum yield of $\bullet OH$ generation by nitrite (unitless).

Column 5: p°_{Sun} . Incident photon flux of sunlight at the water surface ($Einstein\ cm^{-2}\ s^{-1}\ nm^{-1}$).

Column 6: Φ . Photolysis quantum yield of the substrate (unitless).

Column 7: ϵ . Molar absorption coefficient of the substrate ($M^{-1} cm^{-1}$).

Column 8: A_w . Water absorbance over a 1 cm path length (cm^{-1}).

Note that data in columns 1-5 are the same for all input files, those in columns 6,7 are referred to the relevant substrate. Column 8 reports the water spectrum if available. Therefore, if the absorption spectrum of water from the surface layer of the relevant water body has been measured, it can be placed as A_w in column 8 (units of cm^{-1}). The measure unit of A_w means that the values to be inserted are those of surface-water absorbance, spectrophotometrically measured with a cuvette having an optical path length of 1 cm. This is usually not the case, as such a path length is often too short to enable a precise measurement of water absorbance. If absorbance is measured with a cuvette having longer path length (e.g. 5 cm or 10 cm), to obtain A_w one should divide the measured absorbance by e.g. 5 or 10, respectively.

If the water spectrum is not available, one should enter “-1” in all the cells of column 8. In this case, the absorption spectrum of water will be modelled on the basis of the DOC (or NPOC) value (entered in *plotgraph* and *savetable*, vide *infra*), as $A_1(\lambda) = (0.45 \pm 0.04) \cdot NPOC \cdot e^{-(0.015 \pm 0.002) \cdot \lambda}$.

In column 6 it is possible to enter the photolysis quantum yield of the substrate as a function of wavelength, if available. If not, as it often happens, it is also possible to insert a constant value in all the column lines. Another possibility is to put “-1” throughout. In this case, the input value of the photolysis quantum yield will be given in the *plotgraph* and *savetable* functions (vide *infra*). The latter possibility allows one to assess the consequences on pollutant photodegradation of a variation of the photolysis quantum yield. In fact, inside *plotgraph* and *savetable* the photolysis quantum yield can be defined as a variable.

The figure in the next page shows how an input file looks like.

Wavelength, nm	ENO3-, M-1 cm-1	ENO2-, M-1 cm-1	phi(NO2-/OH)	p*sun, Einstein/(cm2)/s/nm	phi	EP, M-1 cm-1	Aw, cm-1
292.5	6.92	8.85	0.068	8.25E-17	7.80E-04	1.07E+04	-1
295	7.5	8.9222	0.068	1.64E-16	7.80E-04	9.84E+03	-1
297.5	7.87	8.98	0.068	3.24E-14	7.80E-04	8.96E+03	-1
300	7.9355	9.07599	0.0678	6.46E-14	7.80E-04	7.98E+03	-1
302.5	8	9.14	0.0674	8.41E-13	7.80E-04	6.97E+03	-1
305	7.7	9.29331	0.0668	1.61E-12	7.80E-04	5.92E+03	-1
307.5	7.2	9.44	0.066	4.04E-12	7.80E-04	4.90E+03	-1
310	6.7	9.66443	0.065	6.44E-12	7.80E-04	3.79E+03	-1
312.5	6	9.915	0.0635	1.21E-11	7.80E-04	2.87E+03	-1
315	5.2	10.2527	0.061	1.78E-11	7.80E-04	2.07E+03	-1
317.5	4.3	10.715	0.058	2.26E-11	7.80E-04	1.43E+03	-1
320	3.5	11.2871	0.054	2.74E-11	7.80E-04	9.75E+02	-1
322.5	2.8	11.99	0.051	3.31E-11	7.80E-04	7.28E+02	-1
325	2.1	12.78278	0.047	3.87E-11	7.80E-04	4.60E+02	-1
327.5	1.5	13.67	0.043	4.87E-11	7.80E-04	3.01E+02	-1
330	1	14.60306	0.0375	5.88E-11	7.80E-04	1.97E+02	-1
333.3	0.6	16.05	0.031	5.88E-11	7.80E-04	1.15E+02	-1
340	0	19.1156	0.026	6.63E-11	7.80E-04	9.41E+01	-1
350	0	22.59355	0.025	7.29E-11	7.80E-04	0.00E+00	-1
360	0	22.01905	0.025	7.75E-11	7.80E-04	0.00E+00	-1
370	0	16.61029	0.025	1.03E-10	7.80E-04	0.00E+00	-1
380	0	9.06147	0.025	1.14E-10	7.80E-04	0.00E+00	-1
390	0	3.41239	0.025	1.21E-10	7.80E-04	0	-1
400	0	0.82399	0.025	1.81E-10	7.80E-04	0	-1
410	0	0.17069	0.025	1.93E-10	7.80E-04	0	-1
420	0	0.06963	0.025	2.06E-10	7.80E-04	0	-1
430	0	0.05638	0.025	1.84E-10	7.80E-04	0	-1
440	0	0.05405	0.025	2.28E-10	7.80E-04	0	-1
450	0	0.05132	0.025	2.83E-10	7.80E-04	0	-1
460	0	0	0	2.83E-10	7.80E-04	0	-1
470	0	0	0	2.85E-10	7.80E-04	0	-1
480	0	0	0	3.06E-10	7.80E-04	0	-1
490	0	0	0	2.94E-10	7.80E-04	0	-1
500	0	0	0	2.92E-10	7.80E-04	0	-1
510	0	0	0	3.13E-10	7.80E-04	0	-1
520	0	0	0	2.97E-10	7.80E-04	0	-1
530	0	0	0	3.27E-10	7.80E-04	0	-1
540	(continues below)			3.18E-10	7.80E-04	0	-1
550	0	0	0	3.33E-10	7.80E-04	0	-1

The figure is cut at 550 nm, but the actual wavelength interval is 292.5-800 nm.

It is advisable to have the input .csv file in the same folder as the other Apex files (e.g. in C:\Apex). In the downloaded version the only input file in the folder is “test.csv”. However, input files for some compounds are contained in the “Compounds” folder (C:\Apex\Compounds), from which they should be moved to the Apex folder (copy to C:\Apex) to enable their easy use.

It is useful to spend some words on how the photolysis quantum yield can be dealt with in Apex. The program has been designed to manage the quantum yield at different levels of knowledge by the user. In other words, the user may know the dependence of the quantum yield on the wavelength (“full knowledge”), or just one average value (or maybe the quantum yield is really constant in the wavelength interval of sunlight absorption by the substrate), or nothing at all. Depending on the level of knowledge, Apex enables four different approaches to the problem (but two of them are equivalent):

- 1) If one knows the values of the photolysis quantum yield as a function of wavelength, they can be inserted in the 6th column (labelled “phi”) of the input file. This is the most favourable situation because photolysis will be computed at each wavelength, also considering depth penetration of sunlight at that wavelength and the competition for irradiance between the solute and other solution components at that wavelength.
- 2) If one knows only a single averaged value of the photolysis quantum yield (or if the quantum yield is constant with wavelength), one can enter the same constant value in the whole 6th column of the input file (this is presently the case with the sample .csv files provided in the “Compounds” folder).
- 3) As an alternative to 2), one can put “-1” overall in the 6th column and add the quantum yield value within **plotgraph** or **savetable** (see the next section 5). The result will be exactly the same as in point 2) above.
- 4) If the quantum yield is unknown, one could wish to see how would the substrate transformation kinetics be modified for different possible values of the quantum yield itself. To do so, one should put “-1” in the whole 6th column of the input file and define the quantum yield as a variable within **plotgraph** or **savetable** (see the next section 5).

An important issue is that there is a hierarchy in the quantum yields data. If quantum yield values are inserted both in the input file and in **plotgraph** or **savetable**, the program will read only the values in the .csv input file and ignore the others. Therefore, if one wants to insert the photolysis quantum yield within **plotgraph** or **savetable**, or define it as a variable, it is necessary that the 6th column (“phi”) of the input .csv file has “-1” throughout.

5. Plotgraph and Savetable

These are the two main functions of Apex that users will most frequently access. They are basically two different ways to present the same output data. **Plotgraph** is intended to produce a 3D plot that shows how the selected output parameter (first-order rate constant, half-life time, yield, *vide infra* for the full list) varies as a function of a couple of selected variables (data of water chemistry and depth, reaction rate constants). **Savetable** reports all the possible output parameters as a function of that couple of variables. Users are expected to open either “plograph.m” or “savetable.m” (they can be opened with any text editor, *e.g.* Windows’ Notepad) and modify the editable parts. In fact, all the wavelength-independent input data should be inserted there. The two functions will be described now with more details.

5.1. Plotgraph

Plotgraph consists of a series of input blocks. They deal with variable (X,Y) range, name of input .csv file (which contains all wavelength-dependent information), numerical parameters and output selection. The rest of the **plotgraph** file (beginning from the quantum yields of formation of $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$ from CDOM) should not be modified by most users, unless they are very experienced in both CDOM photochemistry and Octave programming. Warning notices are present in the relevant parts of the code. The various input blocks will now be commented.

5.1.1. Range input

This section appears as follows (Apex entries are here in blue, data to be modified by the user are here highlighted in yellow; note that Apex is widely commented and that all the comments begin with “%”):

```
% =====  
% *** BEGINNING OF RANGE INPUT ***  
  
x=0.01:0.05:5; % Range for the first variable, A:B:C means from A to C with steps of B.  
y=1e-6:1e-6:1e-4; % Range for the second variable.  
  
% *** END OF RANGE INPUT ***  
% =====
```

Some lines below, the user will be asked to select two variables as X and Y of the 3D graph, after which the Z values will be computed and plotted. Here one should select the X and Y range. Note that three numbers should be entered for each variable, separated by colons: they are the minimum value, the step and the maximum value of the variable, respectively. Therefore, “0.01:0.05:5” means from 0.01 to 5 with steps of 0.05. Note that the smaller the step, the more accurate and “coloured” the final plot will be, but computation time will increase accordingly. In most cases the

actual choice will be a compromise between scientific requirements, aesthetics, processor speed and available time.

5.1.2. Input file prefix

The name of the .csv input file should be given here. Note that “name” means that the relevant file is “name.csv”. The input file should be placed in the same folder as *plotgraph* (for Windows users, the folder may have the path C:\Apex).

```
% =====
% *** INPUT FILE PREFIX ***
% Here you should insert the name of the input file, which reports the spectra of the compound,
% sunlight and water, as well as the photolysis quantum yield.
% file_prefix = prefix for filenames, named <file_prefix> "_LL.csv" ...

file_prefix = "Carbamazepine";

% *** END OF INPUT FILE PREFIX ***
% =====
```

The above entry means that the input file is “Carbamazepine.csv”.

5.1.3. Data input

Here users should specify the numerical values of: water depth, concentration of photochemically relevant parameters (they are to be expressed in **molarity** –**mol L⁻¹**–, with the exception of the NPOC –for many users it is the DOC– that is expressed in **ppm of carbon**, that is, **mg C L⁻¹**),¹³ and reaction rate constants of the studied compound with $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$ (units of **L mol⁻¹ s⁻¹**). It is also possible to model the formation of an intermediate by inserting its (unitless) formation yields from the substrate upon direct photolysis and reaction with $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$. Among the input data, users should choose two variables that will be the X and Y of the 3D plot and that vary within the range defined above. To make the program recognise them, X should be indicated by “-1” and Y by “-2”. The relevant section of the *plotgraph* function is reported in the next page, where the depth *d* is set as X and nitrate concentration as Y.

In the case of *fi_P* (photolysis quantum yield, unitless), the value inserted here will be read by the program only if the relevant column of the input .csv file (column 6, see section 4) has “-1” values throughout. Otherwise, the value inserted here will be ignored and the program will use the data of the input file. The possibility to insert *fi_P* here is interesting if one wants to define *fi_P* as the X or Y variable, and to see the effects of its variation.

The code lines concerning data input are here reported (example data are referred to carbamazepine and to its transformation into acridine, as a function of depth (X) and nitrate (Y)).¹²

¹³ Note that water concentration data are often given in mg L⁻¹ (for nitrate, it may be mg L⁻¹ of N (NO₃-N) or of NO₃, and a similar issue holds for nitrite). Whatever they mean exactly, the mg L⁻¹ data should be converted into molarity (mol L⁻¹) by users to enable proper kinetic calculations.

```
% =====
% *** BEGINNING OF DATA INPUT ***
% NOTE: "-1" denotes the x variable, "-2" the y variable (see above for their ranges)

% d = Water column depth (metres)
d = -1;

% CNO3 = Concentration of NO3- (molarity)
CNO3 = -2;

% CNO2 = Concentration of NO2- (molarity)
CNO2 = 2e-7;

% NPOC = Dissolved Organic Carbon (DOC or NPOC, mgC/L or ppmC)
NPOC = 3.5;

% CCO3 = Concentration of CO3 2- (molarity)
CCO3 = 1e-5;

% CHCO3 = Concentration of HCO3- (molarity)
CHCO3 = 2e-3;

% CBr = Concentration of Br- (molarity)
CBr = 1e-8;

% kP_OH = Reaction rate between P and °OH (units of molarity^-1 seconds^-1, 0 if not available)
kP_OH = 1.8e10;

% kP_CO3 = Reaction rate between P and CO3-° (units of molarity^-1 seconds^-1, 0 if not available)
kP_CO3 = 1e4

% kP_DOM = Reaction rate between P and ³CDOM* (units of molarity^-1 seconds^-1, 0 if not available)
kP_DOM = 7e8

% kP_1O2 = Reaction rate between P and 1O2 (units of molarity^-1 seconds^-1, 0 if not available)
kP_1O2 = 1.9e5

% fi_P = direct photolysis quantum yield of P (unitless, 0 if not available)
fi_P = 7.8e-4;

% y_OH = yield of the intermediate via the °OH pathway (unitless, [formation rate of the intermediate via
°OH]/[transformation rate of P])
y_OH = 0.031;

% y_CO3 = yield of the intermediate via the CO3-° pathway (unitless, [formation rate of the intermediate
via CO3-°]/[transformation rate of P])
y_CO3 = 1e-6;

% y_1O2 = yield of the intermediate via the 1O2 pathway (unitless, [formation rate of the intermediate via
1O2]/[transformation rate of P])
y_1O2 = 1e-6;

% y_3DOM = yield of the intermediate via the 3CDOM* pathway (unitless, [formation rate of the
intermediate via 3CDOM*]/[transformation rate of P])
```

```
y_3DOM = 1e-6;
```

```
% y_Phot = yield of the intermediate via the direct photolysis (unitless, [formation rate of the intermediate via direct photolysis]/[transformation rate of P])
```

```
y_Phot = 0.036;
```

```
% *** END OF DATA INPUT ***
```

```
% =====
```

Note that any of the above variables can be defined as X (-1) or Y (-2), thus it is possible to see the effects of a variation of depth, chemical composition, P reaction rate constants and quantum yield, and formation yields of I from P.

Sets of rate constants have already been measured for some compounds, and some available values are reported as a table in the Appendix.

5.1.4. Output selection

In this section, users define the Z variable of the 3D plot. There is a choice between 36 different variables, namely half-life times *via* the different photochemical processes (direct photolysis and reaction with $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$), first-order rate constants of substrate transformation, steady-state concentrations of $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$ (these are independent of the chosen substrate), rate constants and yields of intermediate formation, relative role of the different processes in substrate transformation and intermediate formation (fraction accounted for by $\cdot\text{OH}$, $\text{CO}_3^{\cdot-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$), fraction of $\cdot\text{OH}$ formation accounted for by nitrate, nitrite and CDOM (which can also be used to compute model errors, *vide infra*). The variable choice is done by inserting the corresponding number.

```
% =====
```

```
% *** BEGINNING OF OUTPUT SELECTION ***
```

```
% The function returns results as a vector in the following order
```

```
% 1) t_OH = The half-life time of P with .OH in Summer Sunny Days (SSD)
```

```
% 2) t_CO3 = The half-life time of P with CO3-. in Summer Sunny Days (SSD)
```

```
% 3) t_1O2 = The half-life time of P with 1O2 in Summer Sunny Days (SSD)
```

```
% 4) t_3DOM = The half-life time of P with CDOM* in Summer Sunny Days (SSD)
```

```
% 5) t_Phot = The half-life time of P by direct photolysis in Summer Sunny Days (SSD)
```

```
% 6) t_tot = The overall half-life time of P in Summer Sunny Days (SSD)
```

```
% 7) k_OH = The first-order rate constant of P for reaction with .OH (1/SSD)
```

```
% 8) k_CO3 = The rate constant of P for reaction with CO3-. (1/SSD)
```

```
% 9) k_1O2 = The rate constant of P for reaction with 1O2 (1/SSD)
```

```
% 10) k_3DOM = The rate constant of P for reaction with CDOM* (1/SSD)
```

```
% 11) k_Phot = The rate constant of P upon direct photolysis (1/SSD)
```

```
% 12) k_tot = The overall rate constant for P degradation (1/SSD)
```

```
% 13) coOH = The steady-state [.OH] in mol/L (22 w/m2 UV irradiance)
```

```
% 14) coCO3 = The steady-state [CO3-.] in mol/L (22 w/m2 UV irradiance)
```

```
% 15) co1O2 = The steady-state [1O2] in mol/L (22 w/m2 UV irradiance)
```

```
% 16) co3DOM = The steady-state [CDOM*] in mol/L (22 w/m2 UV irradiance)
```

```
% 17) f_OH = The first-order rate constant of intermediate formation upon reaction of P with .OH (1/SSD)
```

```
% 18) f_CO3 = The rate constant of intermediate formation upon reaction of P with CO3-. (1/SSD)
```

```
% 19) f_1O2 = The rate constant of intermediate formation upon reaction of P with 1O2 (1/SSD)
```



```

% 20) f_3DOM = The rate constant of intermediate formation upon reaction of P with CDOM* (1/SSD)
% 21) f_Phot = The rate constant of intermediate formation from P by direct photolysis (1/SSD)
% 22) f_tot = The overall rate constant of intermediate formation (1/SSD)
% 23) y_tot = Overall formation yield of the intermediate from P
% 24) role_OH_P = Fraction of P transformation that is accounted for by .OH
% 25) role_CO3_P = Fraction of P transformation that is accounted for by CO3-.
% 26) role_1O2_P = Fraction of P transformation that is accounted for by 1O2
% 27) role_3DOM_P = Fraction of P transformation that is accounted for by 3DOM
% 28) role_Phot_P = Fraction of P transformation that is accounted for by direct photolysis.
% 29) role_OH_I = Fraction of intermediate formation that is accounted for by .OH
% 30) role_CO3_I = Fraction of intermediate formation that is accounted for by CO3-.
% 31) role_1O2_I = Fraction of intermediate formation that is accounted for by 1O2.
% 32) role_3DOM_I = Fraction of intermediate formation that is accounted for by 3DOM.
% 33) role_Phot_I = Fraction of intermediate formation that is accounted for by direct photolysis.
% 34) NO3_OH = Fraction of .OH formation accounted for by nitrate
% 35) NO2_OH = Fraction of .OH formation accounted for by nitrite
% 36) DOM_OH = Fraction of .OH formation accounted for by CDOM)
% Select the variable to be plotted (es: var_to_plot = 6, means t_tot will be plotted).

```

```
var_to_plot = 12;
```

```
% *** END OF OUTPUT SELECTION ***
```

```
% =====
```

With $d = -1$, $CNO_3 = -2$ and $var_to_plot = 12$, k_{tot} will be plotted as a function of depth and nitrate concentration. With all the above choices, a plot will be obtained of the first-order transformation rate constant of carbamazepine as a function of depth and nitrate concentration, with constant $0.2 \mu\text{M}$ nitrite, 3.5 mg C L^{-1} DOC, 2 mM bicarbonate, $10 \mu\text{M}$ carbonate and 10 nM bromide.

MOST USERS WILL END HERE THEIR EDITING OF PLOTGRAPH. The following section contains the quantum yields of generation of $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$ by CDOM. They should be modified only if reliable data are available for the particular system under study. In all other cases, it is better not to alter the existing values.

5.1.5. Quantum yields ($\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$)

If data describing a particular water body are available, quantum yields could be entered by the user in this section. Note that the formation rate of $\text{CO}_3^{\bullet-}$ upon carbonate oxidation by $^3\text{CDOM}^*$ also depends on the carbonate concentration, thus in this case the quantum yield has a different meaning than in the others. This issue should be considered when inserting user data.

The meaning of the relevant variables is as follows:

qyieldOH_CDOM	Quantum yield of $\bullet\text{OH}$ formation by CDOM
qyieldIO2_CDOM	Quantum yield of $^1\text{O}_2$ formation by CDOM
qyieldTriplet_CDOM	Quantum yield of $^3\text{CDOM}^*$ formation by CDOM
carbonateyieldCO3_CDOM	It describes the formation of $\text{CO}_3^{\bullet-}$ by $^3\text{CDOM}^*$ and CO_3^{2-} . It also depends on carbonate concentration. The formula of $\text{CO}_3^{\bullet-}$ formation rate is as follows: $R_{\text{CO}_3\text{CDOM}} = \text{carbonateyieldCO3_CDOM} \cdot \text{CCO}_3 \cdot \text{PaCDOM}$

The relevant lines of the code are reported below.

```
% -----
% === INPUT OF QUANTUM YIELD VALUES FOR REACTIVE SPECIES PHOTOPRODUCTION BY
% CDOM (ONLY FOR EXPERT USERS!!!) ===
% NOTE: MODIFY THESE VALUES ONLY IF YOU DEFINITELY KNOW WHAT YOU ARE
% DOING!!!!

qyieldOH_CDOM = 3e-5;
carbonateyieldCO3_CDOM = 6.5e-3;          % The relevant equation is: R_CO3_CDOM =
carbonateyieldCO3_CDOM * CCO3 * PaCDOM
qyieldIO2_CDOM = 1.25e-3;
qyieldTriplet_CDOM = 1.28e-3;

% === END OF INPUT OF QUANTUM YIELD VALUES
% -----
```

The rest of the **plotgraph** function makes the 3D plot. It should not be modified, unless users are expert in Octave programming.

5.2 Savetable

The function **savetable** is very similar to **plotgraph**, with the difference that it returns the output in the form of a numerical table instead of a 3D plot. The input features are very similar to those already seen for **plotgraph**: the code for *Range input*, *Input file prefix* and *Data input* is exactly the same, including the choice of X and Y variables. **Savetable** does **not** include the *Output selection* section, because the table that is generated reports the data for all the 36 output variables. Such a table file contains 38 columns, namely X, Y and t_OH...DOM_OH. The same issues as for **plotgraph** apply to the *Quantum yields* section (5.1.5).

The table in the following page reports the names of the output variables (in the order they appear in the file and grouped by typology: half-life times, first-order rate constants etc.) as well as a brief description.

<i>Variable</i>	<i>Description</i>
t_OH	Half-life time of P degradation by $\bullet\text{OH}$ (SSD)
t_CO3	Half-life time of P degradation by $\text{CO}_3^{\bullet-}$ (SSD)
t_1O2	Half-life time of P degradation by $^1\text{O}_2$ (SSD)
t_3DOM	Half-life time of P degradation by $^3\text{CDOM}^*$ (SSD)
t_Phot	Half-life time of P degradation by photolysis (SSD)
t_tot	Overall half-life time of P degradation (SSD)
k_OH	First-order rate constant of P degradation by $\bullet\text{OH}$ (SSD^{-1})
k_CO3	First-order rate constant of P degradation by $\text{CO}_3^{\bullet-}$ (SSD^{-1})
k_1O2	First-order rate constant of P degradation by $^1\text{O}_2$ (SSD^{-1})
k_3DOM	First-order rate constant of P degradation by $^3\text{CDOM}^*$ (SSD^{-1})
k_Phot	First-order rate constant of P degradation by photolysis (SSD^{-1})
k_tot	Overall first-order rate constant of P degradation (SSD^{-1})
coOH	Steady-state [$\bullet\text{OH}$] (mol L^{-1} , 22 W m^{-2} UV irradiance)
coCO3	Steady-state [$\text{CO}_3^{\bullet-}$] (mol L^{-1} , 22 W m^{-2} UV irradiance)
co1O2	Steady-state [$^1\text{O}_2$] (mol L^{-1} , 22 W m^{-2} UV irradiance)
co3DOM	Steady-state [$^3\text{CDOM}^*$] (mol L^{-1} , 22 W m^{-2} UV irradiance)
f_OH	First-order rate constant of I formation by $\bullet\text{OH}$ (SSD^{-1})
f_CO3	First-order rate constant of I formation by $\text{CO}_3^{\bullet-}$ (SSD^{-1})
f_1O2	First-order rate constant of I formation by $^1\text{O}_2$ (SSD^{-1})
f_3DOM	First-order rate constant of I formation by $^3\text{CDOM}^*$ (SSD^{-1})
f_Phot	First-order rate constant of I formation by photolysis (SSD^{-1})
f_tot	Overall first-order rate constant of I formation (SSD^{-1})
y_tot	Overall formation yield of I from P (unitless)
role_OH_P	Role of $\bullet\text{OH}$ in P degradation (fraction of total reaction, unitless)
role_CO3_P	Role of $\text{CO}_3^{\bullet-}$ in P degradation (fraction of total reaction, unitless)
role_1O2_P	Role of $^1\text{O}_2$ in P degradation (fraction of total reaction, unitless)
role_3DOM_P	Role of $^3\text{CDOM}^*$ in P degradation (fraction, unitless)
role_Phot_P	Role of direct photolysis in P degradation (fraction, unitless)
role_OH_I	Role of $\bullet\text{OH}$ in I formation (fraction of total reaction, unitless)
role_CO3_I	Role of $\text{CO}_3^{\bullet-}$ in I formation (fraction of total reaction, unitless)
role_1O2_I	Role of $^1\text{O}_2$ in I formation (fraction of total reaction, unitless)
role_3DOM_I	Role of $^3\text{CDOM}^*$ in I formation (fraction of total reaction, unitless)
role_Phot_I	Role of photolysis in I formation (fraction of total reaction, unitless)
NO3_OH	Fraction of $\bullet\text{OH}$ produced by nitrate photolysis (unitless)
NO2_OH	Fraction of $\bullet\text{OH}$ produced by nitrite photolysis (unitless)
DOM_OH	Fraction of $\bullet\text{OH}$ produced by CDOM (unitless)

The **savetable** function creates an output table. To do so one has to run **savetable** within Octave, which will be explained in the next chapter. The figure below shows how the output file looks like.

X	Y	t_OH	t_CO3	t_1O2	t_3DOM	t_Phot	t_tot	k_OH	k_CO3	k_1O2	k_3DOM	k_Phot	k_tot
0.1	0.1	3.321679	16089151	2542855	903.0025	7.261395	2.273373	0.208674	4.31E-08	2.73E-07	0.000768	0.095456	0.304898
0.1	0.2	3.427707	32757483	1273247	452.1475	7.279061	2.318394	0.202219	2.12E-08	5.44E-07	0.001533	0.095225	0.298977
0.1	0.3	3.533256	49984294	850044.3	301.8623	7.296737	2.361908	0.196178	1.39E-08	8.15E-07	0.002296	0.094994	0.293469
0.1	0.4	3.63833	67750475	638442.4	226.7196	7.314423	2.403963	0.190512	1.02E-08	1.09E-06	0.003057	0.094764	0.288335
0.1	0.5	3.742933	86038366	511481	181.6339	7.332117	2.444605	0.185188	8.06E-09	1.36E-06	0.003816	0.094536	0.283542
0.1	0.6	3.847067	1.05E+08	426839.8	151.5766	7.349821	2.483881	0.180176	6.61E-09	1.62E-06	0.004573	0.094308	0.279058
0.1	0.7	3.950736	1.24E+08	366381.6	130.1071	7.367534	2.521834	0.175448	5.58E-09	1.89E-06	0.005328	0.094081	0.274858
0.1	0.8	4.053943	1.44E+08	321037.8	114.0049	7.385256	2.558506	0.170981	4.82E-09	2.16E-06	0.00608	0.093856	0.270919
0.1	0.9	4.156692	1.64E+08	285770.2	101.4809	7.402987	2.593939	0.166755	4.22E-09	2.43E-06	0.00683	0.093631	0.267218
0.1	1	4.258986	1.85E+08	257556	91.46166	7.420726	2.628171	0.162749	3.75E-09	2.69E-06	0.007579	0.093407	0.263738
0.1	1.1	4.360828	2.06E+08	234471.5	83.26404	7.438475	2.66124	0.158949	3.37E-09	2.96E-06	0.008325	0.093184	0.26046
0.1	1.2	4.462222	2.27E+08	215234.3	76.43265	7.456232	2.693184	0.155337	3.05E-09	3.22E-06	0.009069	0.092962	0.257371
0.1	1.3	4.56317	2.49E+08	198956.6	70.6522	7.473998	2.724039	0.1519	2.78E-09	3.48E-06	0.009811	0.092741	0.254456
0.1	1.4	4.663677	2.72E+08	185004.2	65.6975	7.491772	2.753838	0.148627	2.55E-09	3.75E-06	0.0106	0.09252	0.251702
0.1	1.5	4.763744	2.95E+08	172911.9	61.40338	7.509555	2.782615	0.145505	2.35E-09	4.01E-06	0.0112	0.09230	0.249099
0.1	1.6	4.863376	3.18E+08	162331.1	57.646	7.527347	2.810403	0.142524	2.18E-09	4.27E-06	0.012	0.09208	0.246636
0.1	1.7	4.962575	3.41E+08	152995.1	54.33064	7.545146	2.837232	0.139675	2.03E-09	4.53E-06	0.0127	0.09186	0.244304
0.1	1.8	5.061344	3.65E+08	144696.3	51.38361	7.562954	2.863132	0.136949	1.90E-09	4.79E-06	0.01349	0.09165	0.242094
0.1	1.9	5.159687	3.89E+08	137270.9	48.74678	7.58077	2.888133	0.134339	1.78E-09	5.05E-06	0.014219	0.091435	0.239998
0.1	2	5.257606	4.14E+08	130588	46.3736	7.598594	2.912263	0.131837	1.67E-09	5.31E-06	0.014947	0.09122	0.23801
0.1	2.1	5.355105	4.39E+08	124541.6	44.22641	7.616426	2.935548	0.129437	1.58E-09	5.57E-06	0.015673	0.091007	0.236122
0.1	2.2	5.452186	4.65E+08	119044.7	42.2744	7.634266	2.958016	0.127132	1.49E-09	5.82E-06	0.016396	0.090794	0.234328
0.1	2.3	5.548852	4.9E+08	114025.8	40.4921	7.652114	2.979691	0.124917	1.41E-09	6.08E-06	0.017118	0.090582	0.232624
0.1	2.4	5.645107	5.16E+08	109425	38.85831	7.669969	3.000599	0.122787	1.34E-09	6.33E-06	0.017838	0.090372	0.231003
0.1	2.5	5.740954	5.43E+08	105192.2	37.3552	7.687832	3.020762	0.120737	1.28E-09	6.59E-06	0.018556	0.090162	0.229461
0.1	2.6	5.836394	5.7E+08	101285	35.96769	7.705703	3.040204	0.118763	1.22E-09	6.84E-06	0.019271	0.089952	0.227994
0.1	2.7	5.931431	5.97E+08	97667.18	34.68295	7.723581	3.058947	0.11686	1.16E-09	7.10E-06	0.019985	0.089744	0.226597
0.1	2.8	6.026068	6.24E+08	94307.69	33.48995	7.741467	3.077013	0.115025	1.11E-09	7.35E-06	0.020697	0.089537	0.225266
0.1	2.9	6.120308	6.52E+08	91179.85	32.37921	7.75936	3.094423	0.113254	1.06E-09	7.60E-06	0.021407	0.08933	0.223999
0.1	3	6.214154	6.8E+08	88260.47	31.3425	7.77726	3.111196	0.111543	1.02E-09	7.85E-06	0.022115	0.089125	0.222791
0.1	3.1	6.307607	7.08E+08	85529.4	30.37266	7.795167	3.127352	0.109891	9.79E-10	8.10E-06	0.022821	0.08892	0.22164

Note that, for readability issues, only 12 of the whole 36 output variables (one variable per column, in addition to those chosen as X and Y) are shown in the figure above.

In some cases, however, one just needs to predict what is going to happen in a particular environment. Therefore, just one output line (corresponding to a definite set of values of water chemical composition and depth) is required. To do so, one still has to choose two variables as X and Y, but it is possible to make these variable assume a single value. For instance, suppose to choose depth and NPOC as X and Y, respectively. After entering where relevant in **savetable** the concentration values of nitrate, nitrite, bicarbonate, carbonate and bromide, if the water body has d = 5 m and NPOC = 3 mg C / L, the following input values should be inserted:

```
% =====
% *** BEGINNING OF RANGE INPUT ***

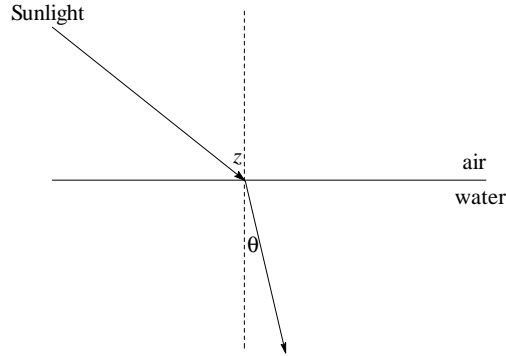
x=5:5:5; % Range for the first variable, A:B:C means from A to C with steps of B.
y=3:3:3; % Range for the second variable.

% *** END OF RANGE INPUT ***
% =====
```

The output file will contain just one line (and all the columns related to the 38 output variables, of course), corresponding to X=5 and Y=3.

5.3. Correction for the solar zenith angle

When considering the path length travelled by sunlight in lake water, one should take into account the solar zenith angle (z) and the refraction of sunlight at the air-water interface. Light reflection at the interface also takes place, but it is of lesser importance and can be neglected.¹⁴ The geometry of irradiation can be represented by the scheme below.



The solar zenith angle z (horizontal system of coordinates) is a function of sun declination δ (geocentric equatorial system of coordinates) and of the hour angle τ . The sun hour angle is defined as the difference between sun's right ascension (geocentric equatorial system of coordinates) and the right ascension of a star on the local meridian. At local noon (when sun is on the local meridian) it is $\tau_{\text{sun}} = 0$. Furthermore, every 1 h difference from the local noon gives $\tau \sim 15^\circ$. This means that after 3 h from local noon, the sun has $\tau \sim 45^\circ$. Assume ϕ as the latitude of the place and (δ, τ) for the sun as above. The following equation holds for the solar zenith angle:¹⁵

$$\cos z = \cos \delta \cos \tau \cos \phi + \sin \delta \sin \phi \quad (50)$$

Water has refraction index $n \sim 1.34$ that undergoes relatively limited variation with wavelength. It is $\sin z = n \sin \theta$, from which the following relationship can be obtained between the path length l of sunlight and the water column depth d : $d = l \cos \theta = l \sqrt{1 - (\sin \theta)^2}$.¹⁴ Therefore, for depth d and solar zenith angle z the optical path length l of sunlight inside the water body would be expressed as follows:

$$l = \frac{d}{\sqrt{1 - (\sin \theta)^2}} = \frac{d}{\sqrt{1 - (n^{-1} \sin z)^2}} \quad (51)$$

This means that water depth could be corrected by a factor $\psi = \left(\sqrt{1 - (n^{-1} \sin z)^2} \right)^{-1}$ ($\psi > 1$) that depends on latitude, hour and season. The following plots report the values of ψ that would be observed at different latitudes and months (they are calculated for the 15th day of each month), at

¹⁴ R.G. Zepp, D.M. Cline, Rates of direct photolysis in aquatic environment. Environ. Sci. Technol. 11 (1977) 359-366.

¹⁵ O. Montenbruck, T. Pflieger, Astronomy on the Personal Computer, 2nd Edition. Springer, Berlin, 1994.

the solar noon ($\tau_{\text{sun}} = 0$) and at ± 3 h from noon ($\tau_{\text{sun}} \sim \pm 45^\circ$), which would constitute a reasonable daily average in many cases. Calculations of z were carried out with the *Perseus* software.¹⁶

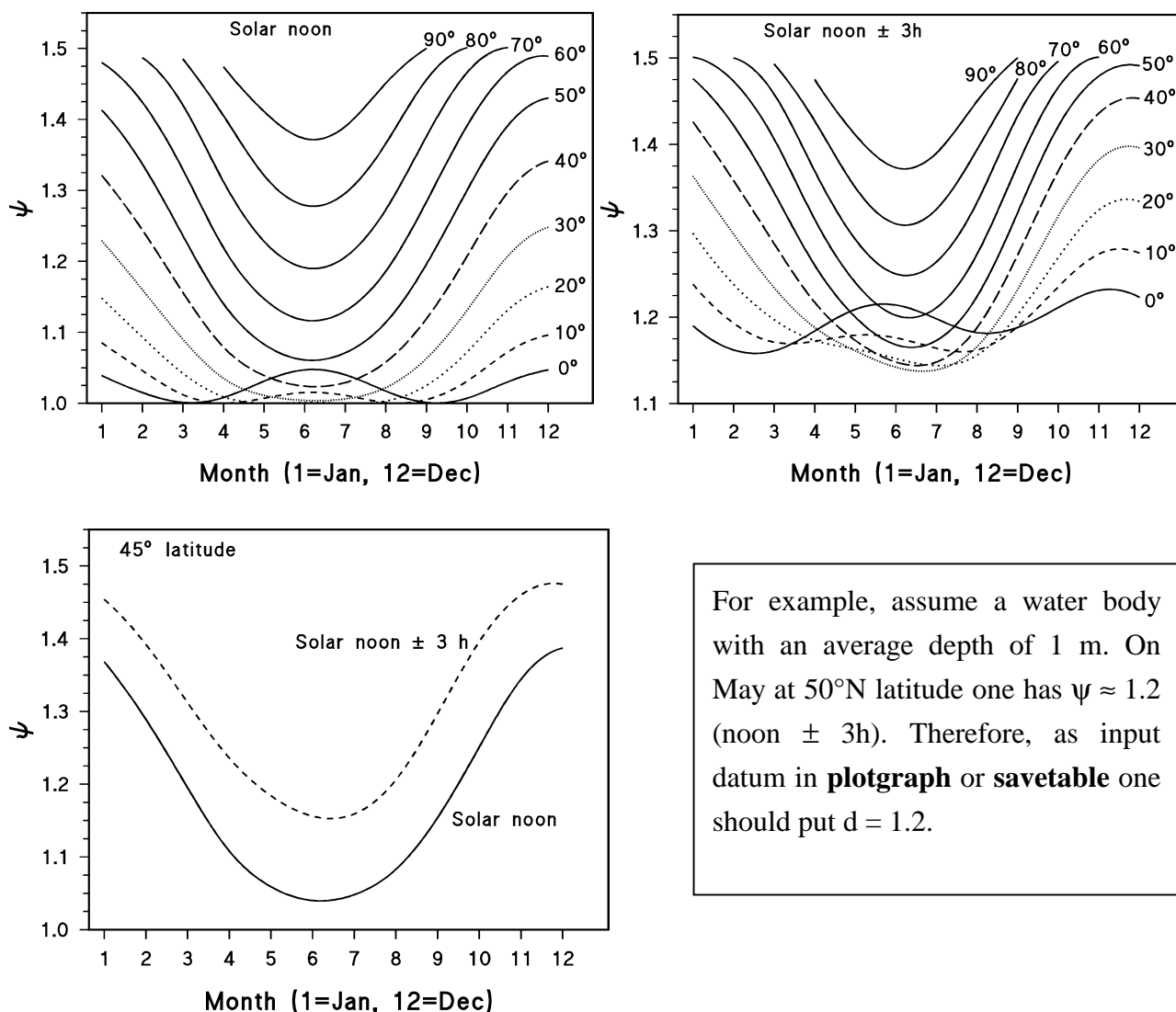


Figure 2. Values of ψ as a function of month and latitude, for the local solar noon and for solar noon ± 3 h. In the upper plots the latitude value is specified near each curve. The 45° latitude is highlighted because it is the standard one used in the model. In the case of noon ± 3 h the calculations were carried out for 3 pm; in the case of 9 am the symmetry of the curves would be opposite. However, differences are much lower than other uncertainties associated to the model.

Note that correcting for the solar zenith angle could not be enough to take the latitude effects into account. For latitude values that are very different from 45° the sunlight spectrum might be quite different than that used in the model and reported in Figure 1, in particular in the UV region. Therefore, a different and more appropriate value for sunlight $p^\circ(\lambda)$ should be used in the input file. Also note that the significance attributed here to a “day”, as far as sunlight irradiance is concerned, would be largely lost in polar regions where sunlight irradiation can be either continuous or absent.

¹⁶ F. Riccio, 2009. <http://www.perseus.it>.

6. Running Plotgraph and Savetable under Octave

When starting Octave, a DOS-like windows appears with some notices and finally a prompt, which in the 3.2.4 version reads as follows:

```
octave-3.2.4.exe:1>
```

It is possible to enter commands at the prompt. First of all, if the Apex files are in the “Apex” folder under disk C (path: “C:\Apex”), one should call that folder. The command to be entered (followed by “↵”) is:

```
octave-3.2.4.exe:1>cd c:\Apex
```

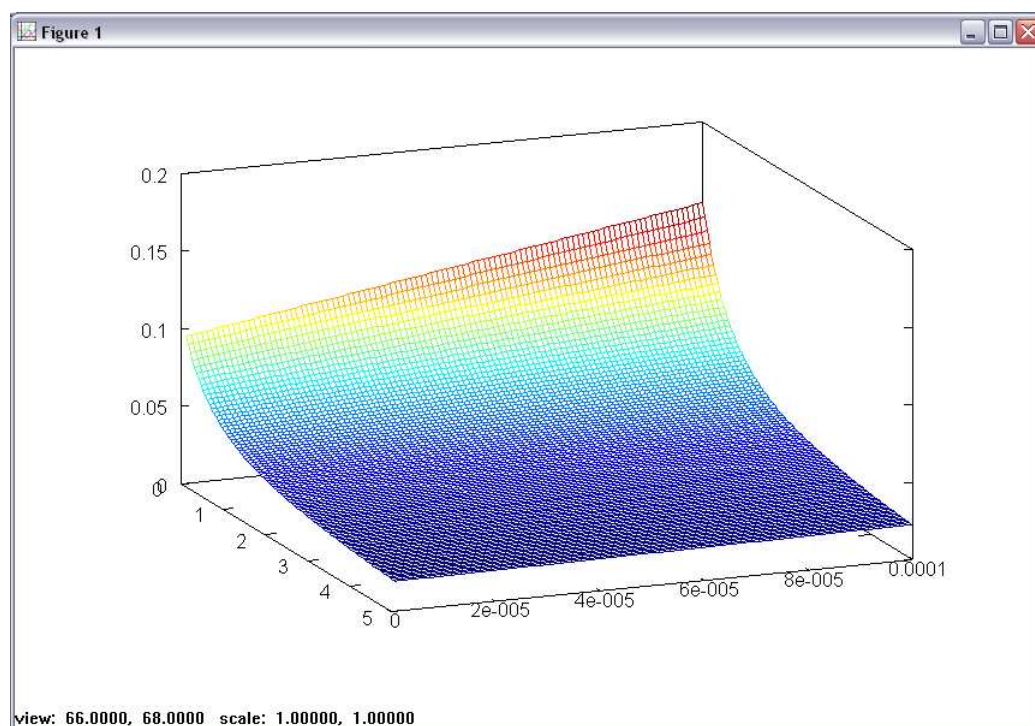
The prompt will now be updated as `octave-3.2.4.exe:2>`, and it is possible to launch Apex calculations. In particular, *plotgraph* and *savetable* can be run here.

6.1. Plotgraph

The easiest way to plot a graph is to have it on the screen, which can be done by entering the following command (always with “↵” at the end):

```
octave-3.2.4.exe:2>plotgraph()
```

Note that the command is case sensitive, and that “plotgraph” has no capital letters. The 3D plot appears in a window and can be rotated for better view, to obtain *e.g.* the following result (**X = d**, **Y = NO₃⁻**, **Z = phototransformation rate constant, k_{tot}**) with the input data of section 5.1 (first-order transformation rate constant of carbamazepine as a function of depth and nitrate concentration, with 0.2 μM nitrite, 3.5 mg C L⁻¹ DOC, 2 mM bicarbonate, 10 μM carbonate, 10 nM bromide):



A finer grid (the figure above adopted a 100×100 one) will usually give a better aesthetic result, but the computer time needed to perform it should be taken into account. Unfortunately, it is not possible to label the axes. Anyway, the vertical one is always the chosen output variable.

The only way to transform the output in a figure file is to make a print of the screen (Alt+Print or Shift+Print) and to paste it in a graphics file, which is a low-resolution option. As an alternative, a .pdf figure file (*e.g.* filename.pdf) can be generated by entering the following command (followed by “↵”):

```
octave-3.2.4.exe:3>plotgraph("filename.pdf")
```

Note the “” around the file name. Obviously, any file name can be given. The advantage is that a usable figure file with better resolution is obtained, but no further rotation is possible. From this point of view, *plotgraph* is a good way to have a quick glance at the general trend of Z vs. (X,Y), but to obtain a nice high-resolution plot one should make use of *savetable*.

6.2. Savetable

The *savetable* function returns a table with the X,Y values in the chosen range and all the possible output variables in 36 columns. The first line of the file reports the column titles. The table file is in a csv-like format, and the file name is to be specified when entering the command. For instance, to create the table filename.csv one should enter the following (plus “↵”):

```
octave-3.2.4.exe:3>savetable("filename.csv")
```

An important issue is that the name of the output .csv file has to be different from the input file name, otherwise the input file will be overwritten.

The output file thus obtained can be the starting point to make a 3D plot with an appropriate software. In this way, one can obtain 3D graphs with fewer limitation compared to the *plotgraph* function.

6.3. Calculation of model errors

The model calculations are unavoidably subject to an uncertainty that combines both the errors on the photochemical kinetics parameters of the substrate P (direct photolysis quantum yield and second-order reaction rate constants with $\bullet\text{OH}$, $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$) and the errors on experimentally derived data of surface-water photochemistry (quantum yields of transient formation from CDOM, nitrate and nitrite and scavenging rate constants by DOM). Details of the equations used for error calculation are reported in Appendix. To make calculation of the errors easier, an Excel file is provided with Apex (C:\Apex\Apex_Errors.xls) and returns absolute and relative errors on all the output parameters. Such parameters should be inserted in the file by copying and pasting a whole line of the output file generated by the *savetable* function.

The way the Apex_Errors.xls file looks like is shown in the picture below (note that the file continues on the right).

The screenshot shows the Apex_Errors.xls Excel file with several annotations:

- Red box:** Photochemical kinetics parameters of the substrate (to be entered by user) and associated errors: photolysis quantum yield, reaction rate constants with photogenerated transients, formation yield of intermediate.
- Blue box:** Fixed relative errors, which in most cases should not be modified.
- Green box:** A whole line from a *savetable* output file should be pasted here to replace the existing one. Error calculations will be carried out on those numbers.
- Yellow cells:** Cells for user input, including reaction rate constants ($k_{\text{P_OH}}$, $k_{\text{P_CO}_3}$, $k_{\text{P_DOM}}$, $k_{\text{P_IO}_2}$), photolysis quantum yield (fi_P), and formation yield of intermediate (y_OH , y_CO_3 , y_DOM , y_IO_2).
- Blue oval:** Relative errors for various parameters (e.g., $\text{reler_NO}_3\text{_OH}$, $\text{reler_NO}_2\text{_OH}$, reler_CDOM_OH , reler_CDOM_CO_3 , reler_CDOM_IO_2 , reler_CDOM_3DOM) which are usually not modified.
- Green box:** A line from an output file to be pasted into the 'Copy here' section.
- Red box:** Absolute and relative errors associated to the output parameters.

Copy here	X	Y	t_OH	t_CO3	t_IO2	t_3DOM	t_Phot	t_tot	k_OH	k_CO3	k_IO2	k_3DOM	k_Phot	k_tot
Copy here	0.01	1.00E-06	4.4158691	317070912	50834436945	99.28600366	14.58357	3.2776329	0.156967	2.19E-09	1.36E-11	0.0063913	0.047529	0.211476

Calculation results	Parameters	t_OH	t_CO3	t_IO2	t_3DOM	t_Phot	t_tot	k_OH	k_CO3	k_IO2	k_3DOM	k_Phot	k_tot
Parameters		4.416E+00	3.171E+08	5.083E+10	9.929E+01	1.458E+01	3.278E+00	1.570E-01	2.186E-09	1.364E-11	6.381E-03	4.753E-02	2.115E-01
Absolute errors		1.149E+00	9.899E+07	2.389E+10	3.839E+01	2.917E+00	8.222E-01	4.084E-02	6.825E-10	6.409E-12	2.699E-03	9.506E-03	5.305E-02

The user should enter data in the yellow cells (photochemical kinetics parameters of the substrate, including -if available- intermediate formation) and paste where indicated a whole line of an output file of the *savetable* function.

6.4. Seasonal corrections at mid latitude

The standard time unit used in the model output is the SSD, summer sunny day, corresponding to fair-weather 15 July at 45°N latitude. Therefore, half life times are expressed in SSD units and first-order rate constants in SSD^{-1} . The results would thus apply to mid-latitude summertime conditions.

If an (approximated) insight is needed into the different behaviour that a compound may have at mid latitude in different seasons, it is possible to take into account the variations of sunlight intensity in the different months of the year. Assume $p^\circ(\lambda)$ as the incident spectral photon flux density of sunlight at mid latitude in a given month of the year (15th of that month).³ The incident photon flux P_o can be calculated as the integral over wavelength of $p^\circ(\lambda)$ over different spectral ranges: 290-320 nm (UVB), 320-400 nm (UVA), and 300-450 nm where most absorption of sunlight by CDOM takes place. The July results are equivalent to a SSD and the results for the other months can be normalised to those of July. Therefore, one can obtain a SSD-normalised photon flux \wp° for the relevant spectral range, which represents the numerical value by which rate constants should be multiplied and half-life times divided to obtain representative photoreactivity values in a given month. The equations used to calculate \wp° are reported below.

$$[P^\circ]_{\text{month}} = \int_{\lambda} [p^\circ(\lambda)]_{\text{month}} d\lambda \quad (52)$$

$$[\wp^\circ]_{\text{month}} = \frac{[P^\circ]_{\text{month}}}{[P^\circ]_{\text{July}}} \quad (53)$$

The following Table reports the values of \wp° for the different months of the year at mid latitude, for three spectral ranges. They are the values by which rate constants should be **multiplied** and half-life time **divided** to obtain the seasonal corrections. Note that $\wp^\circ = 1$ at 15 July (SSD).

Month	SSD-normalised photon flux \wp° (mid latitude)		
	UVB (300-320 nm)	UVA (320-400 nm)	300-450 nm
January	0.0673	0.197	0.214
February	0.168	0.352	0.370
March	0.389	0.596	0.604
April	0.720	0.862	0.860
May	0.924	0.979	0.966
June	1.05	1.03	1.01
July	1.00	1.00	1.00
August	0.985	0.934	0.928
September	0.596	0.664	0.671
October	0.303	0.421	0.439
November	0.101	0.220	0.238
December	0.040	0.129	0.143

The ϕ° values reported in the previous table are referred to different spectral ranges that affect different photosensitisers. In fact, the UVB values can be applied to nitrate photolysis, the UVA ones to nitrite and those at 300-450 nm to CDOM. In the case of reactions induced by $^1\text{O}_2$ and $^3\text{CDOM}^*$ that are produced by CDOM, rate constants should be multiplied by the ϕ° values at 300-450 nm (and half-life times divided by the same values). In the case of $^{\bullet}\text{OH}$ that is produced by nitrate, nitrite and CDOM, the three different contributions should be corrected by the UVB, UVA and 300-450 nm values, respectively. Note that the relative contributions of nitrate, nitrite and CDOM to $^{\bullet}\text{OH}$ generation are given by the output variables NO3_OH, NO2_OH and DOM_OH, respectively, in both *plotgraph* and *savetable*. The radical $\text{CO}_3^{\bullet-}$ is mostly produced by oxidation of carbonate and bicarbonate by $^{\bullet}\text{OH}$, thus the corrections for $\text{CO}_3^{\bullet-}$ are the same as for $^{\bullet}\text{OH}$. Finally, in the case of direct photolysis the correction would depend on the spectral range where the relevant compound mostly absorbs sunlight (UVB, UVA or right into the visible). Depending on compound absorption, the most relevant ϕ° value should be chosen.

To make these calculations a bit easier, an Excel file is provided in the main Apex folder (C:\Apex\APEX_season.xls). The file is made up of three sheets named “UVB”, “UVA” and “300-450 nm”, to be chosen depending on where the pollutant mostly absorbs radiation. In each sheet there is the possibility to paste a whole line copied from an output file of *savetable*, which is referred to a whole set of environmental conditions (see Section 5.2 for such an output .csv file). For instance, the “UVB” sheet looks like as follows (the others are almost identical):

These data should not be modified

A whole line from a *savetable* output file should be pasted here

USE THIS SHEET IF THE POLLUTANT MOSTLY ABSORBS SUNLIGHT IN THE UVB REGION

PLEASE DO NOT MODIFY THESE ENTRIES

	UVB	UVA	300-450 nm
January	0.0673	0.197	0.214
February	0.168	0.352	0.370
March	0.389	0.596	0.604
April	0.720	0.862	0.860
May	0.924	0.979	0.966
June	1.05	1.03	1.01
July	1.00	1.00	1.00
August	0.985	0.934	0.928
September	0.596	0.664	0.671
October	0.303	0.421	0.439
November	0.101	0.220	0.238
December	0.040	0.129	0.143

Copy and paste an entire line from an output .csv file to replace the line of numbers below (the output files are those generated by SAVETABLE)

X	Y	t OH	t CO3	t 1O2	t 3DOM	t Phot	t tot	k OH	k CO3	k 1O2	k 3DOM	k Phot	k tot	coOH	
Paste here =>	1	1.00E-06	5.65575	20.6232	579.58	37.733	21.9666	3.34391	0.12256	0.03361	0.0012	0.01837	0.03155	0.20729	3.35E-16

Calculation results

January	3.05E+01	1.11E+02	2.71E+03	1.76E+02	3.26E+02	1.96E+01	2.27E-02	6.24E-03	2.56E-04	3.93E-03	2.12E-03	3.53E-02	6.22E-17
February	1.69E+01	6.15E+01	1.57E+03	1.02E+02	1.31E+02	1.07E+01	4.11E-02	1.13E-02	4.43E-04	6.00E-03	5.30E-03	6.49E-02	1.12E-16
March	9.82E+00	3.58E+01	9.60E+02	6.25E+01	5.65E+01	6.08E+00	7.06E-02	1.94E-02	7.22E-04	1.11E-02	1.23E-02	1.14E-01	1.93E-16
April	6.67E+00	2.43E+01	6.74E+02	4.39E+01	3.05E+01	4.03E+00	1.04E-01	2.85E-02	1.03E-03	1.58E-02	2.27E-02	1.33E-01	3.85E-16
May	5.82E+00	2.12E+01	6.00E+02	3.91E+01	2.38E+01	3.47E+00	1.19E-01	3.27E-02	1.16E-03	1.77E-02	2.92E-02	1.77E-01	4.95E-16
June	5.49E+00	2.00E+01	5.74E+02	3.74E+01	2.09E+01	3.24E+00	1.26E-01	3.46E-02	1.21E-03	1.86E-02	3.31E-02	1.86E-01	5.15E-16
July	5.66E+00	2.08E+01	5.80E+02	3.77E+01	2.20E+01	3.34E+00	1.23E-01	3.36E-02	1.20E-03	1.84E-02	3.16E-02	1.84E-01	5.05E-16
August	6.03E+00	2.20E+01	6.25E+02	4.07E+01	2.23E+01	3.54E+00	1.15E-01	3.15E-02	1.11E-03	1.70E-02	3.11E-02	1.70E-01	4.85E-16
September	8.60E+00	3.14E+01	8.64E+02	5.62E+01	3.69E+01	5.15E+00	8.06E-02	2.21E-02	8.02E-04	1.23E-02	1.88E-02	1.35E-01	2.21E-16
October	1.38E+01	5.02E+01	1.32E+03	8.60E+01	7.25E+01	8.42E+00	5.03E-02	1.38E-02	5.25E-04	8.06E-03	9.56E-03	8.23E-02	1.38E-16
November	2.70E+01	9.84E+01	2.44E+03	1.59E+02	2.17E+02	1.71E+01	2.57E-02	7.05E-03	2.85E-04	4.37E-03	3.19E-03	4.06E-02	7.03E-17
December	4.66E+01	1.70E+02	4.05E+03	2.64E+02	5.49E+02	3.01E+01	1.49E-02	4.08E-03	1.71E-04	2.63E-03	1.26E-03	2.30E-02	4.07E-17

Continues to the right =>

Output data (for July they are the same as the *savetable* line)

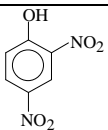
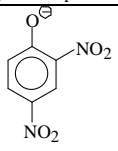
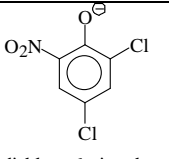
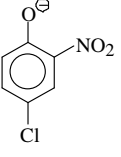
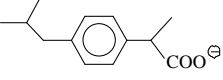
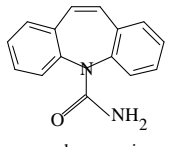
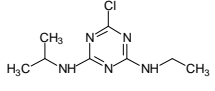
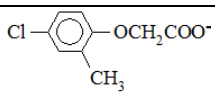
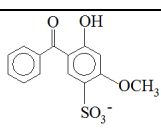
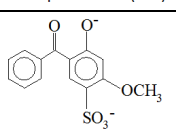
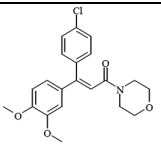
In this way, one can get at a glance on how would the pollutant transformation kinetics (or the kinetics of intermediate formation, or the steady-state concentrations of photoinduced transients) be modified in different seasons than summer. Also note that in the figure of the previous page the view of the sheet is cut at the right margin (the actual sheet continues to the right to include all the output variables).

Two important issues should be considered when using APEX_season.xls:

- 1) Data processing is approximate, in particular as far as the direct photolysis of the pollutant is concerned;
- 2) The corrections are approximately valid only under mid-latitude conditions. In different regions one would need different correction factors.

Anyway, the combination of the seasonal correction described here and of the correction for the solar zenith angle (see Section 5.4) can give insight into seasonality effect on the photochemistry of surface waters. To additionally correct for the solar zenith angle in a given month one should take the relevant ψ value from Figure 2, multiply by ψ the depth input value to be inserted in **savetable**, run **savetable** and paste a line of the output file into APEX_season.xls. The reading of the relevant month gives the approximated changes in photochemical reactivity compared to the standard conditions.

A) Reaction rate constants and photolysis quantum yields of selected xenobiotics

Compound	Φ	$k_{P, \cdot OH}, M^{-1} s^{-1}$	$k_{P, CO_3^{\cdot -}}, M^{-1} s^{-1}$	$k_{P, ^1O_2}, M^{-1} s^{-1}$	$k_{P, ^3CDOM^*}, M^{-1} s^{-1}$
 2,4-dinitrophenol	$(8.1 \pm 0.4) \cdot 10^{-5}$	$(1.76 \pm 0.05) \cdot 10^9$	Negligible	Probably negligible	Probably negligible
 2,4-dinitrophenolate	$(3.4 \pm 0.2) \cdot 10^{-5}$	$(2.33 \pm 0.11) \cdot 10^9$	Negligible	Probably negligible	Probably negligible
 2,4-dichloro-6-nitrophenolate	$(4.53 \pm 0.78) \cdot 10^{-6}$	$(2.8 \pm 0.3) \cdot 10^9$	Negligible	$(3.7 \pm 1.4) \cdot 10^9$	$(1.36 \pm 0.09) \cdot 10^8$
 2-nitro-4-chlorophenolate	$(1.27 \pm 0.22) \cdot 10^{-5}$	$(1.09 \pm 0.09) \cdot 10^{10}$	Negligible	$(2.15 \pm 0.38) \cdot 10^7$	$(5.90 \pm 0.43) \cdot 10^8$
 ibuprofen, anionic form	0.33 ± 0.05	$(1.0 \pm 0.3) \cdot 10^{10}$	Negligible	$(6.0 \pm 0.6) \cdot 10^4$	$(9.7 \pm 0.2) \cdot 10^9$
 carbamazepine	$(7.8 \pm 1.8) \cdot 10^{-4}$	$(1.8 \pm 0.2) \cdot 10^{10}$	Negligible	$(1.9 \pm 0.1) \cdot 10^5$	$(7.0 \pm 0.2) \cdot 10^8$
 atrazine	$(1.58 \pm 0.19) \cdot 10^{-2}$	$(2.7 \pm 0.3) \cdot 10^9$	Negligible	$< 4 \cdot 10^4$	$(1.43 \pm 0.07) \cdot 10^9$
 MCPA (anionic form)	$\frac{(2.3 \pm 0.7) \cdot 10^{-5} + (4.3 \pm 0.1) \cdot 10^{-6} \text{NPOC}}{(4.1 \pm 1.3) \cdot 10^{-5} + 1.4 \cdot 10^{-5} \text{NPOC}}$	$(6.6) \cdot 10^9$	Negligible	Probably negligible	Probably negligible
 Benzophenone-4 (HA ⁻)	$(3.2 \pm 0.6) \cdot 10^{-5}$	$(1.3 \pm 0.2) \cdot 10^{10}$	Negligible	Probably negligible	Probably negligible
 Benzophenone-4 (A ²⁻)	$(7.0 \pm 1.3) \cdot 10^{-5}$	$(1.5 \pm 0.2) \cdot 10^{10}$	Negligible	Probably negligible	Probably negligible
 Dimethomorph	$(2.6 \pm 0.4) \cdot 10^{-5}$	$(2.6 \pm 0.4) \cdot 10^{10}$	Negligible	$(8.5 \pm 0.3) \cdot 10^5$	$(1.6 \pm 0.2) \cdot 10^9$

B) Model errors

Input data of substrate reactivity and intermediate formation are (or should be) affected by errors, model assumptions/equations have an uncertainty, and the model output is affected by error as well.

The following table reports the names of variables that are affected by errors, and the names of variables representing **absolute errors**. The colour code highlights input data (light yellow), and **output data** related to the degradation kinetics of the substrate P (light green), steady-state concentrations of reactive transients (pink), intermediate formation kinetics and yield (grey), role of photochemical processes in P transformation (orange), and role of photochemical processes in intermediate (I) formation (light blue).

Quantity	Description	Absol. error
kP_OH	Reaction rate constant (2 nd order) between P and $\bullet\text{OH}$ ($\text{M}^{-1} \text{s}^{-1}$)	er_kP_OH
kP_CO3	Reaction rate constant (2 nd order) between P and $\text{CO}_3^{\bullet-}$ ($\text{M}^{-1} \text{s}^{-1}$)	er_kP_CO3
kP_DOM	Reaction rate constant (2 nd order) between P and $^3\text{CDOM}^*$ ($\text{M}^{-1} \text{s}^{-1}$)	er_kP_DOM
kP_1O2	Reaction rate constant (2 nd order) between P and $^1\text{O}_2$ ($\text{M}^{-1} \text{s}^{-1}$)	er_kP_1O2
fi_P	Photolysis quantum yield of P (unitless)	er_fi_P
y_OH	Yield of the intermediate I via the $\bullet\text{OH}$ pathway (unitless)	er_y_OH
y_CO3	Yield of the intermediate I via the $\text{CO}_3^{\bullet-}$ pathway (unitless)	er_y_CO3
y_1O2	Yield of the intermediate I via the $^1\text{O}_2$ pathway (unitless)	er_y_1O2
y_DOM	Yield of the intermediate I via the $^3\text{CDOM}^*$ pathway (unitless)	er_y_DOM
y_Phot	Yield of the intermediate I via direct photolysis (unitless)	er_y_Phot
t_OH	Half-life time of P degradation by $\bullet\text{OH}$ (SSD)	er_t_OH
t_CO3	Half-life time of P degradation by $\text{CO}_3^{\bullet-}$ (SSD)	er_t_CO3
t_1O2	Half-life time of P degradation by $^1\text{O}_2$ (SSD)	er_t_1O2
t_3DOM	Half-life time of P degradation by $^3\text{CDOM}^*$ (SSD)	er_t_3DOM
t_Phot	Half-life time of P degradation by photolysis (SSD)	er_t_Phot
t_tot	Overall half-life time of P degradation (SSD)	er_t_tot
k_OH	First-order rate constant of P degradation by $\bullet\text{OH}$ (SSD^{-1})	er_k_OH
k_CO3	First-order rate constant of P degradation by $\text{CO}_3^{\bullet-}$ (SSD^{-1})	er_k_CO3
k_1O2	First-order rate constant of P degradation by $^1\text{O}_2$ (SSD^{-1})	er_k_1O2
k_3DOM	First-order rate constant of P degradation by $^3\text{CDOM}^*$ (SSD^{-1})	er_k_3DOM
k_Phot	First-order rate constant of P degradation by photolysis (SSD^{-1})	er_k_Phot
k_tot	Overall first-order rate constant of P degradation (SSD^{-1})	er_k_tot
coOH	Steady-state [$\bullet\text{OH}$] (mol L^{-1} , 22 W m^{-2} UV irradiance)	er_coOH
coCO3	Steady-state [$\text{CO}_3^{\bullet-}$] (mol L^{-1} , 22 W m^{-2} UV irradiance)	er_coCO3
co1O2	Steady-state [$^1\text{O}_2$] (mol L^{-1} , 22 W m^{-2} UV irradiance)	er_co1O2
co3DOM	Steady-state [$^3\text{CDOM}^*$] (mol L^{-1} , 22 W m^{-2} UV irradiance)	er_co3DOM
f_OH	First-order rate constant of I formation by $\bullet\text{OH}$ (SSD^{-1})	er_f_OH
f_CO3	First-order rate constant of I formation by $\text{CO}_3^{\bullet-}$ (SSD^{-1})	er_f_CO3
f_1O2	First-order rate constant of I formation by $^1\text{O}_2$ (SSD^{-1})	er_f_1O2
f_3DOM	First-order rate constant of I formation by $^3\text{CDOM}^*$ (SSD^{-1})	er_f_3DOM
f_Phot	First-order rate constant of I formation by photolysis (SSD^{-1})	er_f_Phot
f_tot	Overall first-order rate constant of I formation (SSD^{-1})	er_f_tot
y_tot	Overall formation yield of I from P (unitless)	er_y_tot
role_OH_P	Role of $\bullet\text{OH}$ in P degradation (fraction of total reaction, unitless)	er_role_OH_P
role_CO3_P	Role of $\text{CO}_3^{\bullet-}$ in P degradation (fraction of total reaction, unitless)	er_role_CO3_P
role_1O2_P	Role of $^1\text{O}_2$ in P degradation (fraction of total reaction, unitless)	er_role_1O2_P
role_3DOM_P	Role of $^3\text{CDOM}^*$ in P degradation (fraction, unitless)	er_role_3DOM_P
role_Phot_P	Role of direct photolysis in P degradation (fraction, unitless)	er_role_Phot_P
role_OH_I	Role of $\bullet\text{OH}$ in I formation (fraction of total reaction, unitless)	er_role_OH_I
role_CO3_I	Role of $\text{CO}_3^{\bullet-}$ in I formation (fraction of total reaction, unitless)	er_role_CO3_I
role_1O2_I	Role of $^1\text{O}_2$ in I formation (fraction of total reaction, unitless)	er_role_1O2_I
role_3DOM_I	Role of $^3\text{CDOM}^*$ in I formation (fraction of total reaction, unitless)	er_role_3DOM_I
role_Phot_I	Role of photolysis in I formation (fraction of total reaction, unitless)	er_role_Phot_I

Equations that compute the generation and scavenging of reactive transients by (C)DOM, nitrate and nitrite are affected by errors. Therefore, there are a number of constants that represent the **relative errors** on the quantum yields of $\bullet\text{OH}$ production by nitrate, nitrite and CDOM, on $\bullet\text{OH}$ scavenging by DOM, and on quantum yields of $\text{CO}_3^{\bullet-}$, $^1\text{O}_2$ and $^3\text{CDOM}^*$ generation by CDOM.^{1,10,11} They are listed in the table below.

<i>Name of constant</i>	<i>Value</i>	<i>Description</i>
reler_NO3_OH	0.05	Relative error on quantum yield of $\bullet\text{OH}$ production by nitrate
reler_NO2_OH	0.08	Relative error on quantum yield of $\bullet\text{OH}$ production by nitrite
reler_CDOM_OH	0.13	Relative error on quantum yield of $\bullet\text{OH}$ production by CDOM
reler_DOM_OH	0.15	Relative error on $\bullet\text{OH}$ scavenging by DOM
reler_CDOM_CO3	0.32	Relative error on $\text{CO}_3^{\bullet-}$ production by CDOM
reler_CDOM_1O2	0.27	Relative error on quantum yield of $^1\text{O}_2$ production by CDOM
reler_CDOM_3DOM	0.22	Relative error on quantum yield of $^3\text{CDOM}^*$ production by CDOM

Absolute errors on the input data (reaction rate constants and quantum yield of P, intermediate formation yields) should be provided by the user. Based on these errors and on those reported in the above table, **Apex_Errors.xls** computes the absolute errors of the output variables. Before reporting the equations by which absolute errors were calculated, a Table is provided to describe other variables that are used to compute the errors.

<i>Name of variable</i>	<i>Description</i>
ROH_NO3	Formation rate of $\bullet\text{OH}$ by nitrate
ROH_NO2	Formation rate of $\bullet\text{OH}$ by nitrite
ROH_CDOM	Formation rate of $\bullet\text{OH}$ by CDOM
ROH_TOT	Total formation rate of $\bullet\text{OH}$
carbonateyieldCO3_CDOM	Quantum yield of $\text{CO}_3^{\bullet-}$ generation by CDOM

1) Steady-state [$\bullet\text{OH}$]

$$er_coOH = coOH \left\{ \frac{\left[reler_NO3_OH \times ROH_NO3 + reler_NO2_OH \times ROH_NO2 + \right.}{ROH_TOT} + reler_CDOM_OH \times ROH_CDOM \left. \right] + reler_DOM_OH \right\}$$

2) Steady-state [$\text{CO}_3^{\bullet-}$]

$$er_coCO3 = \frac{coCO3^* er_coOH}{coOH}$$

3) Steady-state [$^1\text{O}_2$]

$$er_colO2 = colO2 \times reler_CDOM_1O2$$

4) Steady-state [³CDOM*]

$$er_co3DOM = co3DOM \times reler_CDOM_3DOM$$

5) Half-life time of P ([•]OH) and first-order rate constant of P transformation ([•]OH).

$$er_k_OH = k_OH \times \left(\frac{er_kP_OH}{kP_OH} + \frac{er_coOH}{coOH} \right)$$

$$er_t_OH = t_OH \times \frac{er_k_OH}{k_OH}$$

6) Half-life time of P (CO₃^{•-}) and first-order rate constant of P transformation (CO₃^{•-}).

$$er_k_CO3 = k_CO3 \times \left(\frac{er_kP_CO3}{kP_CO3} + \frac{er_coCO3}{coCO3} \right)$$

$$er_t_CO3 = t_CO3 \times \frac{er_k_CO3}{k_CO3}$$

7) Half-life time of P (¹O₂) and first-order rate constant of P transformation (¹O₂).

$$er_k_1O2 = k_1O2 \times \left(\frac{er_kP_1O2}{kP_1O2} + reler_CDOM_1O2 \right)$$

$$er_t_1O2 = t_1O2 \times \frac{er_k_1O2}{k_1O2}$$

8) Half-life time of P (³CDOM*) and first-order rate constant of P transformation (³CDOM*).

$$er_k_3DOM = k_3DOM \times \left(\frac{er_kP_DOM}{kP_DOM} + reler_CDOM_3DOM \right)$$

$$er_t_3DOM = t_3DOM \times \frac{er_k_3DOM}{k_3DOM}$$

9) Half-life time of P (photolysis) and first-order rate constant of P transf. (photolysis).

$$er_k_Phot = k_Phot \times \left(\frac{er_fi_P}{fi_P} \right)$$

$$er_t_Phot = t_Phot \times \frac{er_k_Phot}{k_Phot}$$

10) Half-life time of P (total) and first-order rate constant of P transformation (total).

$$er_k_tot = er_k_OH + er_k_CO3 + er_k_1O2 + er_k_3DOM + er_k_Phot$$

$$er_t_tot = t_tot \times \frac{er_k_tot}{k_tot}$$

11) Intermediate formation rate constant ($\bullet OH$)

$$er_f_OH = f_OH \times \left(\frac{er_y_OH}{y_OH} + \frac{er_k_OH}{k_OH} \right)$$

12) Intermediate formation rate constant ($CO_3^{\bullet-}$)

$$er_f_CO3 = f_CO3 \times \left(\frac{er_y_CO3}{y_CO3} + \frac{er_k_CO3}{k_CO3} \right)$$

13) Intermediate formation rate constant (1O_2)

$$er_f_1O2 = f_1O2 \times \left(\frac{er_y_1O2}{y_1O2} + \frac{er_k_1O2}{k_1O2} \right)$$

14) Intermediate formation rate constant ($^3CDOM^*$)

$$er_f_3DOM = f_3DOM \times \left(\frac{er_y_3DOM}{y_3DOM} + \frac{er_k_3DOM}{k_3DOM} \right)$$

15) Intermediate formation rate constant (photolysis)

$$er_f_Phot = f_Phot \times \left(\frac{er_y_Phot}{y_Phot} + \frac{er_k_Phot}{k_Phot} \right)$$

16) Intermediate formation rate constant (total)

$$er_f_tot = er_f_OH + er_f_CO3 + er_f_1O2 + er_f_3DOM + er_f_Phot$$

17) Intermediate formation yield (total)

$$er_y_tot = y_tot \times \left(\frac{er_f_tot}{f_tot} + \frac{er_k_tot}{k_tot} \right)$$

18) Fraction of substrate (P) degradation accounted for by $\bullet OH$

$$er_role_OH_P = role_OH_P \times \left(\frac{er_k_OH}{k_OH} \right)$$

19) Fraction of substrate (P) degradation accounted for by $\text{CO}_3^{\cdot-}$

$$er_role_CO3_P = role_CO3_P \times \left(\frac{er_k_CO3}{k_CO3} \right)$$

20) Fraction of substrate (P) degradation accounted for by $^1\text{O}_2$

$$er_role_1O2_P = role_1O2_P \times \left(\frac{er_k_1O2}{k_1O2} \right)$$

21) Fraction of substrate (P) degradation accounted for by $^3\text{CDOM}^*$

$$er_role_3DOM_P = role_3DOM_P \times \left(\frac{er_k_3DOM}{k_3DOM} \right)$$

22) Fraction of substrate (P) degradation accounted for by photolysis

$$er_role_Phot_P = role_Phot_P \times \left(\frac{er_k_Phot}{k_Phot} \right)$$

23) Fraction of intermediate (I) formation accounted for by $\cdot\text{OH}$

$$er_role_OH_I = role_OH_I \times \left(\frac{er_f_OH}{f_OH} \right)$$

24) Fraction of intermediate (I) formation accounted for by $\text{CO}_3^{\cdot-}$

$$er_role_CO3_I = role_CO3_I \times \left(\frac{er_f_CO3}{f_CO3} \right)$$

25) Fraction of intermediate formation accounted for by $^1\text{O}_2$

$$er_role_1O2_I = role_1O2_I \times \left(\frac{er_f_1O2}{f_1O2} \right)$$

26) Fraction of intermediate formation accounted for by $^3\text{CDOM}^*$

$$er_role_3DOM_I = role_3DOM_I \times \left(\frac{er_f_3DOM}{f_3DOM} \right)$$

27) Fraction of intermediate formation accounted for by photolysis

$$er_role_Phot_I = role_Phot_I \times \left(\frac{er_f_Phot}{f_Phot} \right)$$