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OECD GUIDELINE FOR TESTING OF CHEMICALS

PROPOSAL FOR A NEW GUIDELINE

Phototransformation of Chemicals in Water - Direct and Indirect Photolysis

INTRODUCTION

1. This guideline provides guidance for conducting phototransformation in water studies to determine the potential effects of solar irradiation on chemical pollutants in surface water. Such studies determine phototransformation kinetics, products, and product pathways resulting from both direct and (as an option or if applicable) indirect aqueous photolysis. It is based on current and /or proposed methods (references 1 through 10) and on relevant literature on environment aqueous photochemistry.
2. A glossary of definitions (11) and symbols/units are provided in Annexes 1 and 2 respectively.

ENVIRONMENTAL SIGNIFICANCE AND USE

3. Chemical pollutants and/or their transformation products that are potentially susceptible to direct and/or indirect photolysis include those that are transported to surface water by direct point discharge and/or by runoff from urban and/or rural areas. Chemical pollutants in surface water also often originate from transformation of other chemicals via hydrolysis, photolysis, and biotransformation.
4. Direct photolysis in natural water involves the transformation of a chemical resulting from the direct absorption of a solar photon (references 12 through 18). Indirect photolysis in natural water sometimes involves the transformation of a chemical due to energy transfer from naturally occurring photosensitizers in electronically excited triplet states (12)(13)(19)(20). However, indirect photolysis more often involves the transformation of a chemical due to reactions with transient oxidants such as hydroxyl radicals, molecular oxygen in a singlet electronic state ("singlet oxygen"), and peroxy radicals (references 12 and 22 through 32). Both triplet state photosensitizers and transient oxidants result from the absorption of solar photons by chromophoric dissolved organic matter (CDOM) and nitrate ion (12)(21)(32)(33)(34).
5. Direct photolysis can be an important dissipation pathway for some chemical pollutants that exhibit significant light absorption above the 295 nm cutoff of solar irradiation at the earth's surface. Indirect photolysis can also be an important dissipation pathway for some chemical pollutants that come in contact with photosensitizers in electronically excited triplet states or with short-lived photochemically generated oxidants such as hydroxyl radicals and singlet oxygen. In some cases both direct and indirect photolysis can contribute significantly to the dissipation of a chemical in natural waters.
6. The direct and indirect phototransformation of chemicals in natural water bodies is a complex process which depends on a number of factors such as:
 - (a) the chemical structure and electronic absorption spectrum of the chemical;

- (b) the concentration, composition, and absorption spectra of CDOM (from which photosensitizers and singlet oxygen arise);
- (c) the concentration of nitrate (the primary source of hydroxyl radicals); and
- (d) the solar photon flux spectrum to which the chemical, CDOM and nitrate are exposed.

7. The solar photon flux spectrum to which a chemical, CDOM, and nitrate are exposed depend on numerous factors including the latitude, season, and the physical and chemical properties of the water body (12)(18)(35)(36). Important properties of the water body which contribute to the attenuation of solar irradiation with depth include the concentration and composition of CDOM and suspended particulates. The mixing and stratification properties of the water will help determine the horizontal and vertical distribution of the chemical, CDOM, and nitrate.

8. The results of phototransformation in water studies are used in conjunction with physical chemical properties and data from other studies (abiotic hydrolysis; biotransformation; adsorption/desorption) to help assess the overall environmental transformation and transport of chemical pollutants. The results of phototransformation in water studies are also used to help develop inputs for environmental fate computer models, and to help develop protocols for conducting other aquatic laboratory and/or aquatic field studies.

PRINCIPLE OF THE STUDY

Scope and approach

9. This test guideline is designed to provide some or all of the following data and/or information depending upon specific needs:

- The quantum yield and resulting estimated direct photolysis rate constants for test chemicals for various types of water bodies (defined by depth and light attenuation), seasons, and latitudes of interest.
- Direct photolysis rate constants for test chemicals determined in the laboratory using filtered xenon arc lamp or sunlight irradiation and extrapolated to natural water. A xenon arc lamp filtered to remove irradiation < 295 nm will be referred to throughout the rest of the document as a filtered xenon arc lamp.
- The net (combined direct and indirect) and indirect photolysis rate constants of one or more test chemicals in a standard simulated natural water (containing humics as a surrogate for CDOM and in some cases, nitrate) and/or in one or more natural waters.
- The transformation pathway and the identities, concentrations, and rates of formation and decline of major phototransformation products resulting from direct photolysis and/or indirect photolysis.

10. This guideline is designed as a tiered approach. Each tier is triggered by the results of the previous tier. Tiered approaches are proposed separately for direct and indirect photolysis tests as shown in Figures 1 and 2, respectively (see Annex 3).

Pseudo first-order kinetics of direct and indirect photolysis

11. The rate of decline of a test chemical in either a direct or indirect photolysis study is generally assumed to follow pseudo first-order kinetics (e.g., time series data are fit to a pseudo first-order kinetics model):

$$\frac{d[C]}{dt} = -k[C] \quad \text{[eq. 1]}$$

The integrated form of equation 1 is:

$$[C] = [C_0] \exp(-kt) \quad \text{[eq. 2]}$$

The ln transformed version of equation 2 is:

$$\ln[C] = \ln[C_0] - kt \quad \text{[eq. 3]}$$

where

- C = test chemical concentration (mol/L)
- C₀ = initial test chemical concentration at time t = 0
- k = pseudo first-order rate constant (1/unit of time)
- t = time
- t_{1/2} = half-life

The pseudo first-order rate constant is determined by using non-linear regression to fit data to equation 2 or using linear regression to fit data to equation 3.

The half-life can be determined by substituting the pseudo first-order rate constant into the following equation:

$$t_{1/2} = \frac{\ln 2}{k_{(d \text{ or } i)}} \quad \text{[eq. 4]}$$

where k_d is the direct photolysis rate constant and k_i is the indirect photolysis rate constant.

Note: In the equations provided in this guideline, units for half-lives, pseudo first-order rate constants and photon fluxes are (for illustrative purposes) given in days, 1/day, and photons/cm²•day, respectively. However, other units of time such as hours or seconds may be used as long as there is consistency within the same equation. Units of concentration are given in mol/L.

Direct photolysis

12. To undergo transformation via direct photolysis, a chemical molecule must first absorb a photon of light. The absorption of a photon by a molecule results in a transition from an electronic ground state to an electronically excited state of the molecule. To be absorbed by the molecule, the energy of the photon (which is inversely proportional to its wavelength) must correspond to the difference between the ground and a possible excited electronic state of the molecule (12). Within the UV-Visible wavelength of interest

(295-800 nm), photons energies range from 150 kJ/mol at 800 nm to slightly greater than 400 kJ/mol at 295 nm (11)(37).

13. The absorption of a photon is a necessary, but often not a sufficient condition, for a molecule to undergo transformation via direct photolysis (12)(14)(37). The absorbed energy must first be sufficient to cause the transformation via bond cleavage, rearrangement, oxidation, or reduction. Then, phototransformation to form new molecular structures must compete with other possible deactivation processes such as quenching, other radiationless processes, and radiative processes. Consequently, the fraction of photon excited molecules that actually undergo phototransformation (e.g. the quantum yield) is generally much less than 1 (usually < 0.1 and sometimes < 0.01) (14)(21). The mechanistic aspects of phototransformation reactions at a molecular level are beyond the scope of this guideline (see reference 38 for further information).

14. It can be shown that for an optically dilute solution (absorbance $A < 0.02$) of a chemical in pure water exposed to polychromatic irradiation above the cutoff of solar irradiation at the earth's surface of 295 nm, the direct photolysis rate constant (assuming the quantum yield is independent of wavelength) is given by (12)(14through 18) (See Annex 4: Derivation of selected equations):

$$k_d = \frac{2.3}{j} \frac{l}{D_{\text{sys}}} \phi \sum_{295}^{800} \epsilon_{\lambda} I_{0\lambda} \quad [\text{eq. 5}]$$

where:

k_d = direct photolysis rate constant (1/day)

ϕ = the quantum yield (independent of wavelength)

ϵ_{λ} = molar absorption coefficient (L/mol•cm; $M^{-1} \cdot \text{cm}^{-1}$) at wavelength λ

$I_{0\lambda}$ = photon flux (photons/cm²•day) over a 1 nm interval centered at wavelength λ

D_{sys} = depth of irradiated system (cm) = volume of irradiated system/incident area

l = light pathlength (cm)

j = conversion factor to make units consistent with the L/mol•cm unit of the molar absorption coefficient and the mol/L unit of concentration = 6.02×10^{20} (L/cm³)(photons/mol)

Note: The term (l/D_{sys}) in equation 5 approximately cancels out for rectangular photolysis cells exposed to irradiation from a filtered xenon arc lamp and for which $D_{\text{sys}} = D_{\text{cell}}$. However, that would not be true for cylindrical photolysis cells or for any photolysis cells exposed to solar irradiation where the pathlength l has a more complicated dependency on D_{cell} . Methods for determining the pathlength of cylindrical cells exposed to filtered xenon-arc lamps are discussed in references 12 and 17. Pathlength determinations as a function of the depth of a system, D_{sys} exposed to solar irradiation are discussed in references 12 and 18. In addition, note that if the quantum yield is not independent of wavelength, it must remain inside of the summation in equation 5.

15. Equation 5 is applicable to solar as well as filtered xenon arc lamp irradiation. However, the following equation is often used to determine the direct photolysis rate constant for optically dilute solutions of test chemicals in pure water in photolysis cells or in near surface, clear natural water exposed to solar irradiation (2)(12) (See Annex 4: Derivations of selected equations):

$$\overline{k}_{d(\text{solar})} = \phi \sum_{295}^{800} \epsilon_{\lambda} L_{\lambda} \quad [\text{eq. 6}]$$

where:

k_d = direct photolysis rate constant (1/day)

ϕ = quantum yield (independent of wavelength)

ϵ_λ = molar absorption coefficient (L/mol•cm) at wavelength λ

L_λ = average daily solar photon flux irradiance (mmol photons/cm²•day) over wavelength interval $\Delta\lambda$ centered at wavelength λ

16. Equations 1, 5 and 6 show that direct photolysis kinetics are theoretically pseudo-first order only if the photon flux remains constant over time. Photon fluxes from filtered xenon arc lamps at any given wavelength remain, in general, relatively constant over time. This is one of the primary advantages in using filtered xenon arc lamps. However, solar photon fluxes at any given wavelength vary cyclically over 24-hour periods. Nevertheless, the data obtained from studies conducted in natural sunlight (in which the rate constant reflects an average over the entire study duration) generally do fit a single, pseudo-first order rate constant model reasonably well. The reason is that changes in the average pseudo first-order rate constant over time as the study progresses is generally relatively small and not systematic. This is particularly valid for studies conducted for one to several weeks or for 2-4 hours mid-day. It may not be as valid for studies lasting 4 hours to several days or for those conducted beyond 30 days.

Summary of the proposed tiered approach for direct photolysis

Tier 1: Theoretical screen

17. Estimate a maximum possible direct photolysis rate constant for the test chemical in the near surface of a clear natural water as follows. Measure the test chemical molar absorption coefficients from 295 nm to 800 nm, and use tabular solar irradiance for summer and 40° or 50° latitude over the same wavelength interval. Estimate a maximum possible direct photolysis rate by assuming the quantum yield in equation 6 is equal to one and by substituting the molar absorption coefficients and tabular solar irradiance values, L_λ into the equation (2)(12). Determine if the estimated maximum possible direct photolysis rate constant would theoretically result in estimated direct photolysis losses greater than 50% of an initial concentration over 30 days/nights. If maximum possible losses are < 50%, no further direct photolysis work is performed, but proceed to Indirect Photolysis Tier 1 (experimental/theoretical screen), if required. If the maximum possible losses \geq 50%, proceed to Direct Photolysis Tier 2 (experimental screen and range finding) or to Direct Photolysis Tier 3 (determination of the quantum yield).

Tier 2 - Experimental screen and range finding

18. Approximately determine the rate of decline in the concentration of the test chemical and corresponding direct photolysis rate constant in buffered pure water exposed to a filtered xenon arc lamp (recommended) or sunlight. Determine if the approximate direct photolysis rate constant would result in estimated direct photolysis losses equal or greater than to 20% of an initial concentration over 30 days/nights in the near surface of a clear natural water body exposed to summer sunlight. If estimated losses are < 20%, no further direct photolysis work is performed, but proceed to Indirect Photolysis Tier 1 (experimental/theoretical screen), if required. If estimated losses \geq 20%, proceed to Direct Photolysis Tier 3 (determination of the quantum yield). If the determination of the quantum yield is not required, proceed to Direct Photolysis Tier 4 (kinetics study).

Tier 3 - Determination of the quantum yield and its use to estimate direct photolysis rate constants

19. Determine the quantum yield for direct photolysis of the test chemical in buffered pure water using monochromatic irradiation (12), polychromatic artificial irradiation (8) or sunlight (2). Once the quantum

yield has been determined, use it as input to computer programs such as GCSOLAR (18) or ABIWAS (35)(36) to help estimate direct photolysis rates for the test chemical applicable to any types of surface waters (defined by depth and light attenuation), seasons, and latitudes of interest (2). If the Direct Photolysis Tier 4 study is potentially applicable, determine if the direct photolysis rate constants estimated from the quantum yield would result in estimated direct photolysis losses greater than or equal to 20% of the initial concentration over 30 days/nights in the near surface of a clear natural water body exposed to sunlight. If the estimated losses are < 20%, no further direct photolysis work is required but proceed to Indirect Photolysis Tier 1 (experimental/theoretical screen), if required. If the estimated losses are ≥ 20%, proceed to the Direct Photolysis Tier 4 kinetics study.

Tier 4 - Kinetics study on the parent and, if applicable, major transformation products

20. Determine the rate of decline in the concentration of the test chemical and corresponding direct photolysis rate constant in buffered pure water exposed to a filtered xenon arc lamp (recommended) or sunlight. If applicable, also identify/quantify and determine the rates of formation and decline of major transformation products. In this guideline, major transformation products are defined as those accounting for ≥ 10% of the applied test chemical at any sampling time.

Indirect Photolysis

21. To undergo transformation via indirect photolysis, the test substance must:

- receive energy from a photosensitizer in an excited electronic triplet state such as various ones generated from the solar irradiation of CDOM (12)(14)(19)(20), or
- react with a photochemically generated oxidant such as a hydroxyl free radical, a singlet oxygen, or an alkylperoxy free radical (references 12 and 21 through 32). Singlet oxygen and alkylperoxy free radicals appear to be generated primarily from the solar irradiation of CDOM in oxygenated natural waters. Some hydroxyl free radicals also appear to originate from the solar irradiation of CDOM. However, the major source of the hydroxyl free radical in natural waters appears to generally be the solar irradiation of nitrate (21).

22. In infrequent cases where the nitrate to nitrite ratio is less than 100 in aerobic surface waters, the photolysis of nitrite (which is present in much lower concentrations than nitrate) may also contribute significantly to the formation of hydroxyl radicals because “nitrite photoproducts OH radicals about 50 times more rapidly than nitrate” (39).

23. The transformation of chemical pollutants in surface waters may also occur via photoredox reactions with soluble and insoluble Fe (III) species, which are commonly present at significant concentrations in many surface waters (40)(41).

24. Indirect photolysis kinetics are actually closer to being second-order than first-order because the rate of decline of the test chemical is generally proportional to the product of the test chemical and sensitizer or photooxidant concentrations (12)(20)(21). However, although transient photooxidant and excited photosensitizer concentrations are very low (typically below 1×10^{-10} M), they can quickly attain quasi steady-state concentrations in irradiated solutions thereby leading to pseudo first-order kinetics (12)(20)(21).

25. In many cases, the net pseudo first-order rate constant for indirect photolysis will reflect the reaction of different molecules with more than one type of sensitizer and/or oxidant:

$$k_{\text{indirect}} = \sum_{j=1}^{j=n} k_{j(2nd)} \left(S_{j(ss)} \text{ or } \text{Ox}_{j(ss)} \right) \quad [\text{eq. 7}]$$

where:

- k_{indirect} = net pseudo first-order indirect photolysis rate constant (1/day)
 $k_{j(2nd)}$ = second order rate constant for the reaction with sensitizer j or oxidant j (L/mol•d)
 $S_{j(ss)}$ = steady state concentration of sensitizer j (mol/L)
 $\text{Ox}_{j(ss)}$ = steady state concentration of oxidant j (mol/L)

Summary of the proposed tiered approach for indirect photolysis

Tier 1 - Experimental and/or theoretical screen

26. Perform an experimental screen in simulated natural water (SNW) containing humics as a surrogate for CDOM, and/or in a simulated natural water containing nitrate as well as humics (SNW-N) and/or in one or more natural waters (NW) and in buffered pure water (PW) (3). Specifications for PW appear in paragraph 68-a. Approximately determine the rate of decline in the concentration of the test chemical in SNW, and/or SNW-N, and/or NW exposed to sunlight to determine if indirect photolysis represents a potentially significant transformation pathway. The use of a xenon lamp light source for indirect photolysis studies is not recommended at this time. Determine if the estimated indirect (not net) photolysis losses over the equivalent of 30 days/nights of sunlight exposure is greater than or equal to 20% of an initial concentration of the test chemical. If the estimated indirect photolysis losses are < 20%, no further indirect photolysis work is performed. If the estimated indirect photolysis losses are $\geq 20\%$, proceed to the Indirect Photolysis Tier 2 (kinetics study).

27. In some cases, it may be possible to supplement the Tier 1 experimental screen with a theoretical screen based on using structure activity relationships (SARs) to estimate rate constants for reaction with photooxidants and information on the typical concentrations of photooxidants in surface water (21).

Tier 2 - Kinetics study on the parent and (if applicable) major transformation products

28. Determine the rate of decline in the concentration of the test chemical and its corresponding net and indirect photolysis rate constants in SNW, and/or SNW-N and/or one or more NWs irradiated with sunlight and in PW. If data on transformation products for indirect photolysis are applicable, identify/quantify major transformation products and determine their rates of formation and decline. In this guideline, major transformation products are defined as those accounting for $\geq 10\%$ of the applied test chemical (percent of applied radioactivity or molar basis) during any part of the study.

APPLICABILITY OF THE TEST GUIDELINE

29. This test guideline is applicable to chemical substances for which analytical methods with sufficient accuracy and precision are available and validated (if required). If data are needed on transformation products, adequate quantitative analytical methods must also be available/developed for them.

30. If a non-ionic test chemical is somewhat susceptible to hydrolysis, the test may still be applicable as long as a dark control is used to account for the hydrolysis rate (2)(4)(5). However, photolysis tests should be conducted at a pH at which the hydrolysis rate of the chemical is minimized (5)(42). The rate

constant determined from the dark controls should be identical to the hydrolysis rate constant and can be subtracted from the overall rate constant determined from the irradiated solutions to give the direct photolysis rate constant. However, in some cases, the desired test chemical may undergo rapid hydrolysis (i.e., hydrolysis half-life of < 1 day) within the environmentally relevant pH range of 5-9 at 20-25°C. In such cases, the photolysis study should instead be conducted on each major hydrolytic product ($\geq 10\%$ of applied) as the test substance.

31. The test is not applicable to highly volatile compounds such as fumigants and some organic solvents. However, in some cases, where the Henry's Law constant of the test chemical and/or anticipated transformation products may indicate the potential for fairly substantial volatilization rates from water, the study may still be applicable provided that precautions are taken. Such precautions include using minimal head-space, adequate sealing in the photolysis cells to minimize volatile losses during the study (2)(4) or trapping. Trapping volatiles becomes more difficult, but preferred, when employing sacrificial sampling on numerous small photolysis cells than when employing aliquot sampling on a smaller number of much larger test vessels. However, with the proper equipment and experimental set-up, it can be done as shown by Ruzo (43).

INFORMATION ON THE TEST SUBSTANCE

32. Before carrying out any of the phototransformation tests, the following information on the test substance should be known, if available:

- (a) Solubility in water [OECD Guideline 105].
- (b) Vapor pressure [OECD Guideline 104]
- (c) Henry's Law Constant*
- (d) Abiotic hydrolysis as a function of pH [OECD Guideline 111]
- (e) *n*-octanol/water partition coefficient [OECD Guidelines 107 and 117]
- (f) $pK_a(s)$ of ionisable substances [OECD Guideline 112]
- (g) Chemical nomenclature (IUPAC and CAS)
- (h) Chemical Abstract Registry Number of the test substance
- (i) Common name(s), if any
- (j) Chemical structure
- (k) Position(s) of radiolabelled atom(s) or other molecular tags (if applicable)
- (l) Isomer purity (if applicable)

Note: The temperatures at which the physical chemical properties listed in the previous paragraph were determined should generally be within the range of $(25 \pm 5)^\circ\text{C}$ and should be specified.

33. If available, the solubility in non-aqueous solvents may be useful in selecting a co-solvent or extractant. Also, the following optional information may be useful for indirect photolysis studies conducted in natural water:

- Aerobic - Anaerobic Transformation in Aquatic Sediment Systems [OECD draft Guideline 308]
- Adsorption / Desorption [OECD Guideline 106]

34. The *n*-octanol/water partition coefficient and aqueous solubility supply some information on the

* Henry's Law constant estimated from solubility in water and vapour pressure or measured. Henry's Law constants for some chemicals may also be found in: <http://webbook.nist.gov/chemistry>

potential of the test chemical to significantly adsorb to glassware and reaction vessels. However, any additional information on the glassware adsorption potential of the test chemical should be known to ensure that such characteristics are taken into account in preparing glassware and reaction vessels for the study.

ANALYTICAL METHODS AND QUALITY CRITERIA

35. The experimenter should develop methods with appropriate accuracy (recovery), precision (reproducibility), and adequate limits of detection (LOD) and quantification (LOQ). In many instances, validation of the analytical methodology may be required. In those cases, the experimenter should be responsible for ensuring that the analytical methods have been validated.

36. The analytical methods that may be used include liquid scintillation counting (LCS) and radiochromatography (radiolabelled substances), high-performance liquid chromatography (HPLC), gas chromatography (GC), gas-liquid chromatography (GLC), and capillary electrophoresis (CE), etc. TLC can also be used for radiolabelled test chemicals, but only if adequate resolution can be achieved and there is no decomposition of the reference standards in the silica plates.

37. When necessary to identify and/or confirm transformation products, the separation methods listed in the preceding paragraph may be coupled with spectrometric methods such as mass spectrometry (MS) and/or Fourier-Transform Infrared spectroscopy (FT-IR). Examples of such couplings include as GC/MS, HPLC/MS, LC/MS-MS, GC/FT-IR or any other adequate techniques.

38. Reference chemicals of potential transformation products may be used for identification (e.g. by co-chromatography). When radiolabelled test substance is used, it may be necessary to use radiolabelled reference chemicals. However, as indicated in the previous paragraph, the identities of major transformation products need to be confirmed preferably by an independent analytical chemistry method such as with MS. Transformation products that cannot be identified from reference chemicals should be elucidated using, for example, MS, NMR and infrared spectroscopy.

39. Parameters that can influence the accuracy and/or precision of the determination of chemical concentrations in aqueous media include the stability of the chemicals in samples during storage, extraction efficiency, analytical separation efficiency in mixtures, and the magnitude of the concentrations with respect to analytical detection and quantification limits.

40. Analytical instrumentation should be periodically calibrated within applicable concentration ranges according to the manufacturer's specifications. If samples are stored prior to analysis, storage stability tests may need to be performed depending upon the storage method and duration. The accuracy and precision of the analytical method should be checked within the expected concentration range. Accuracy can be determined from the recovery percentages of spiked samples. Precision can be determined by replicate analyses of an appropriate percentage of the samples.

41. Regardless of the chosen analytical method, analytical recoveries for radiolabelled test chemicals should fall within 90% and 110% of the applied radioactivity. For non-radiolabelled test chemicals, analytical recoveries of 85 to 115% are desirable.

42. For radiolabelled materials, total mass balance should fall within that range 90% to 110% of the total applied radioactivity (42).

TEST MATERIALS

Test vessels

43. All glassware and reaction vessels/photolysis cells used in the photolysis studies must be sterilized by autoclaving (2)(3)(4)(12). Chemical sterilization is not recommended since chemical reagents may leave residues that could absorb in the 295 to 800 nm region and/or behave as photosensitizers.

Test substance

44. If radiolabelling is used, test chemicals should be labelled at one or more atoms within each stable or relatively stable portion of the molecule. For chemicals containing one or more aromatic rings, one or more atoms in each ring are usually labelled. In addition, one or more atoms on both sides of any linkage thought to be readily susceptible to cleavage should be radiolabelled (42). Radiolabelling is particularly important when there is the need to identify transformation pathways. Radiolabelling does not have to be limited only to ^{14}C . For example, in some cases, ^{32}P can be used in place of or in addition to ^{14}C (42). If mass spectroscopy is used, stable isotopes such as ^{15}N can also be used as molecular tags.

45. Radiolabelled test substances should have radiochemical and chemical purities of 95% or greater (42). Non-radiolabelled test substances should have a chemical purity of 95% or greater (42).

46. If the test chemical consists of more than one geometrical and/or optical isomer, the percentage represented by each isomer should be provided.

47. Pesticide testing should generally be conducted with the active ingredient. The same generally applies to pharmaceutical chemicals. However, in some instances it may be more appropriate to use a formulated product.

48. If the potential loss of the test chemical by volatilization or adsorption to test vessels is of concern or if the identification and quantification of major transformation products are of interest, radiolabeling should be used.

Test media

49. Guidance for preparing test media for direct and indirect photolysis respectively is provided in Annex 5.

Test media for direct photolysis

50. For direct photolysis studies, the test media should be sterilized aqueous buffer solutions at the appropriate pH. The water should be "pure water" (PW). The buffers should be identical or comparable to those used in the hydrolysis studies and should not absorb between 295 and 800 nm or be photosensitizers. Also, the buffers should not adversely affect the solubility of the test chemical.

51. If the test chemical is non-ionizable and is approximately stable to abiotic hydrolysis at pH 7, the buffer used in the direct photolysis study should maintain a pH of approximately 7. However, if the hydrolysis rate of a non-ionizable test chemical at pH 7 is significant, but its hydrolysis rate at pH 5 or 9 is much lower, the buffer used should maintain a pH (within the 5 to 9 range) at which the hydrolysis rate is minimized (42).

52. If the test chemical is appreciably ionic anywhere within a 5 to 9 pH range, the study should be

conducted in one or more aqueous buffers at any of the pH 5, 7, and/or 9. Selection of the pH (s) at which the study should be conducted depends on the electronic absorption spectra at each pH. Spectra showing absorption bands between 295 and 800 nm or shorter wavelengths tailing above 295 nm together with estimates of maximum photolysis rates (Tier 1: Direct Photolysis) are the criteria for selecting the pH(s). Refer to Tier 1, Direct Photolysis for further details.

53. For test chemicals with low aqueous solubility, a co-solvent may be used to prepare the test solution. However, the amount of co-solvent used must be as little as possible and preferably not exceed 1% by volume in the test solution (42). Co-solvent percentages up to 10% may be used, but if more than 10% co-solvent is required to dissolve the test chemical, the study should not be performed. The selected co-solvent must not solvolyse the test chemical, must not absorb in the 295 to 800 nm region, and must not be a photosensitizer. Acetone is an example of a solvent that is a photosensitizer, and should not be used. Acetonitrile is a generally recommended co-solvent.

Test media for indirect photolysis studies

54. The selection of test media for indirect photolysis studies depends on the purpose of the study. The preparation of test media is based on the procedure given in OPPTS 835.5270 guideline (3). Three test media may be used for these studies: (1) SNW (Simulated Natural Water); SNW-N (Simulated Natural Water with Nitrate); and (3) NW (Natural Water). SNW-N may be appropriate for areas where surface waters show strong evidence of nitrate pollution associated with the use of fertilizer and other nitrate-bearing substances. Nitrate has been known to photochemically produce hydroxy radical (21)(22)(26). NW may be important in situations when the understanding of the photochemical behavior of chemicals in actual natural surface waters is of interest.

55. Humic acid or other humic materials may be obtained commercially (Aldrich, Fluka, etc.). Humic and fulvic acid extracted from soils or natural surface water may be used as surrogates for aquatic humic acids (23)(44). Composite data for typical humic acids are available from the International Humic Substances Society (45). The UV-VISIBLE spectra of the selected humic materials in the test media (natural water and/or buffered SNW) should be provided. The absorption spectra of some humic materials are shown in reference 46.

Light sources

56. For direct photolysis studies the recommended light source should be a filtered xenon arc lamp capable of simulating natural sunlight in the 295 to 800 nm region or sunlight (47). For indirect photolysis studies, the only recommended light source at this time is sunlight. The photon flux of the filtered xenon arc lamp as a function of wavelength should be determined at least at the beginning and the end of the study using one or more actinometers and a spectral radiometer if available. If sunlight is used, average daily solar photon fluxes (L_{λ}) as a function of wavelength should be determined for the season and latitude closest to those of the experiment using solar irradiance tables and a spectral radiometer, if available.

57. If a filtered xenon arc lamp is used, the irradiation photon flux incident on the test vessels should be adequate to cause substantial decline of the test chemical over a several day experimental period. The transformation rate constant and corresponding half-life obtained with a filtered xenon arc lamp can be adjusted to solar equivalents from a comparison of solar photon flux to lamp photon flux because of the linear relationship between the transformation rate and photon flux (see equation 14).

58. If sunlight is used, the study should be conducted during the season when and at the latitude where the concentration of the test chemical is expected to be highest in the environment. For pesticides, that would be the season when and the latitude where it is typically applied.

59. If a filtered xenon arc lamp and sacrificial sampling of multiple test vessels are used, an appropriate experimental set-up should be used to ensure that all of the test vessels receive the same incident irradiation flux. Self-contained, commercially available xenon photolysis units in the projection or “working plane” configuration produce uniform fluxes (48)(49a). A commonly used configuration is the “merry-go-round” photochemical reactor (12). Merry-go-round photochemical reactors are commercially available (49a)(49b). Another example of an experimental set-up is shown reference 50. An experimental set-up that includes trapping of volatiles appears in reference (43).

Other photolytic equipment and reagents

60. Photolytic equipment includes:

- Optical cells of appropriate material (generally quartz) and pathlength for measuring UV-VIS spectra.
- Appropriate optical filters to cut-off radiation below 295 nm and above 800 nm.
- When monochromatic irradiation is used in the determination of the quantum yield, the appropriate filter systems must be used to isolate the desired wavelength (12)(47). Monochromatic irradiation at the desired wavelength can also be achieved with a monochromator in conjunction with a suitable polychromatic light source such as a mercury or xenon arc lamp. (Filters for isolating the 313 and 366 nm wavelengths from a mercury arc lamp are discussed in reference 12).
- Specially designed reaction cuvettes/photolysis cells to contain test solutions (exposed and dark control) and chemical actinometers, when needed. The recommended material is quartz.
- Appropriate apparatus designed to contain the light source, filters, sample, holders, reaction vessels/actinometers such as the photochemical “merry-go-round” reactor. Several appropriate designs are commercially available to accommodate specific needs.
- Photometer or spectral radiometer to measure photon flux as a function of wavelength.

61. Photolytic reagents include:

- All of the water used in the direct photolysis tests must be of high purity and free of any absorbing or photosensitizing chemical species. For example, the U.S.EPA OPPTS 835.2210 (2) recommends using reagent water meeting ASTM Type IIA standards, as described in ASTM D1193-99 Standard Specification for Reagent Water (see Annex 5: Test Media). “Milli-Q” water is one example of high purity water. In this guideline, the water used in the preparation of stock, test and buffer solutions is referred as “pure water”.
- Appropriate chemical reagents to be used as actinometers.
- Commercially available, certified humic material for indirect photolysis studies (Fluka; Aldrich).
- Analytical grade NaNO₃
- Appropriate aqueous buffers such as phosphate for pH 7, acetate for pH 5 and borate for pH 9 for compatibility with hydrolysis studies. Phosphate buffers are usually recommended for direct photolysis studies(2)(12).

Analytical equipment and chemical reagents

62. In addition to standard laboratory equipment, the following is required:

- Spectrophotometer to acquire spectral data in the UV-VIS range. For example, single beam, diode array instruments that allow sensitive, rapid acquisition of digitized spectral absorbance data.
- Appropriate analytical instrumentation to measure the concentration of the test substance in exposed and dark control samples, such as HPLC, GLC, TLC, etc.

- Suitable instrumentation for identification purposes, such as MS, HPLC/MS, GC/MS, LC/MS, GC-FTIR, NMR, etc.
- When radiolabelled test substances are used, liquid scintillation counters (LSC) and instrumentation for radiochromatography should be available.
- Appropriate extraction apparatus.
- Equipment to sterilise reaction vessels and other glassware used in the preparation of stock and test solutions.

63. Chemical reagents include:

- Reagent grade chemicals and solvents free of any photosensitizer.
- Scintillation liquid (for radiolabelled chemicals).

64. Analytical references include:

- Test substance reference standards for co-chromatography and/or for other analytical methods.
- Potential transformation products (including hydrolysis products) reference standards for the determination of products, if applicable.

TEST METHODOLOGY

Test conditions

65. The temperature during photolysis studies may vary by as much as 10 degrees but should be maintained within the range of 20 to 30 C. (25 ± 5)°C.

66. The pH of buffered solutions should be maintained within ± 0.5 pH units. The pH should be checked during the course of the study, if feasible.

67. Dark control solutions should be used for all quantum yield determinations and for all direct and indirect photolysis studies.

68. The concentration of the chemical in the test media should never exceed half its solubility. When a co-solvent is needed, it should preferably not exceed 1% by volume in the test solution and never exceed 10% by volume.

69. The initial concentration of the test chemical for quantum yield determinations and direct photolysis studies should be such that the absorbance at any wavelength above 295 nm (maximum absorption wavelength included) is less than 0.02. These optically dilute, also referred to as “optically thin”, solutions generally have a concentration of $< 10^{-4}$ M. Nevertheless, the initial concentration of the test chemical should be at least 10 times greater than the quantification limit of the analytical method.

70. The concentration of the test chemical in simulated (SNW, SNW-N) or natural water (NW) test media should be equivalent to that of optically dilute test solutions in pure water/buffer solutions required for direct photolysis studies.

71. Because oxygen can affect the rates and even pathways of photodegradation reactions, test solutions should be saturated with air at the beginning of the study (4). A buffer solution that has been autoclaved should be given sufficient time to aerate prior to dispensing into the vessels. It is not recommended to autoclave small amounts of buffer in individual vessels because driving the air out may

change the volume.

Study duration, sampling, and replication

72. The study duration should be sufficient to determine the DT₇₅ (two half-lives if decline is first-order) of the test chemical and (if applicable) the formation and decline of major transformation products until they have declined to < 25% of their maximum concentration. However, the maximum study duration should not exceed the equivalent of 30 days/nights of sunlight exposure during an appropriate season and at an appropriate latitude. The "DT₇₅" is defined as the time required for 75% of the initial concentration of test chemical to disappear.

73. Based upon equating photons absorbed by the test chemical per unit volume, the maximum direct photolysis study duration (using continuous filtered xenon arc lamp irradiation) that is equivalent to 30 days/nights of sunlight exposure will be only a few days and is given by (see Annex 4).

$$\text{Max. direct photolysis duration(days)} = 30j \frac{D_{\text{cell}} \sum_{295}^{800} \epsilon_{\lambda} L_{\lambda}}{I_{\text{xenon}} \sum \epsilon_{\lambda} I_{0\lambda(\text{xenon})}} \quad [\text{eq. 8}]$$

where:

30 = 30 days/nights of solar irradiation

D_{cell} = depth of irradiated cell (cm) = volume of irradiated cell/incident area

I_{xenon} = light pathlength in cell exposed to a filtered xenon arc lamp

and other terms same as defined for equations 5 and 6.

Note: For rectangular box cells, the term D_{cell}/I_{xenon} cancels out because I_{xenon} = D_{cell}. However, that will not be true for cylindrical cells (12).

74. Although equation 8 allows for flexibility in choosing an experimental photon flux from a filtered xenon arc lamp, practical considerations somewhat limit the range of experimental fluxes that should be used. In general, it is recommended that the experimental photon flux from a filtered xenon lamp be adjusted to be somewhat comparable to that of sunlight (at noon for short several hour studies or 24 hour average for several day to weeks studies). The reason is the experimental flux should not be so intense that photolytic processes other than those that would occur under natural sunlight are initiated. Also, if the parent is susceptible to hydrolysis at the experimental pH and the hydrolytic products are susceptible to direct photolysis, time should be allowed for them to form.

75. A preliminary range-finding study should be performed to help determine the number of samples to be collected and the timing of their collection. For linear and non-linear regressions on test chemical data in definitive or upper tier tests, the minimum number of samples collected should be five and seven, respectively. The greatest number of samples taken should generally be during the first part of the study where the slope of the concentration versus time series for the test chemical is generally greatest. If an accurate determination of the rates of formation and decline of major transformation products is desired, the number of samples taken should generally be greater and somewhat more dispersed throughout the study duration. The number of sampling times can be less in range finding or lower tier tests.

76. Either aliquot or sacrificial sampling can be used. Sacrificial sampling of entire photolysis cells at each sampling time is often preferred over withdrawing aliquots of test solutions at each sampling time. The reason is that it helps to maintain aseptic conditions and allows for mass balance determinations at

each sampling time. The use of sacrificial sampling is particularly necessary in cases where mass balance determinations are needed such as when the test chemical and/or its transformation products are volatile and/or adsorb strongly to the photolysis cells (5). Future sampling descriptions in this document will be for the generally preferred sacrificial sampling, but aliquot sampling from larger irradiated and dark control reaction vessels is acceptable as long as the resulting mass balance is adequate and aseptic conditions are properly maintained.

77. Replicates (preferably a minimum of three) of each experimental determination of kinetic parameters are recommended to determine variability and reduce uncertainty in the determination of kinetic parameters. However, the uncertainty in the determination of kinetic parameters can also be reduced by increasing the number of sampling intervals within each experiment, particularly when the rates of formation and decline of major transformation products are being determined. In such cases, a minimum of two replicate determinations of kinetic parameters may be adequate. With generally limited resources, the researcher needs to weigh the pros and cons of experimental replication versus increased numbers of sampling times per experiment in designing the study.

Calculations

78. Basic calculations/equations, including the following one used to determine whether going to higher tiers is triggered, are included within the body of the guideline:

$$\% \text{ loss over 30 days / nights solar} = 100 \left\{ 1 - \exp \left[-k_{(solar)} (t = 30d) \right] \right\} \quad [\text{eq. 9}]$$

where:

k_{solar} = pseudo first-order direct or indirect photolysis rate constant for test chemical exposed to solar irradiation (1/day)

79. Calculations/equations for the kinetics of the formation and decline of major photoproducts, and accounting for photobleaching are optional. The necessary non-linear regressions can be readily performed with the use of commercially available spreadsheets and/or statistical software.

Determination of the photon flux from a filtered xenon arc lamp

80. The photon flux from a filtered xenon arc lamp can be determined with the use of low and/or high optical density actinometers alone or preferably in conjunction with a spectral radiometer (51). The advantage in using a spectral radiometer to determine the photon flux is convenience, as it avoids changing actinometers. However, spectral radiometers are expensive and are not always readily available. Furthermore, even if a spectral radiometer is generally used to determine the photon flux, it should be periodically calibrated against photon fluxes determined with actinometers. Calibration is necessary because of the difference between the exposure surface of a spectral radiometer and that of the photolysis cuvette or tubes used to contain the actinometers (51).

81. By determining the monochromatic first-order direct photolysis rate constant for a low optical density actinometer of known quantum yield in PW in a photolysis cell irradiated with monochromatic irradiation, the incident photon flux at the wavelength of the irradiation can be determined from the following equation (51; see Annex 3 - Equation Derivations):

$$I_{0\lambda(xenon)} = \frac{j D_{cell} k_{d\lambda(act)}}{2.3 I_{xenon} \phi_{act} \epsilon_{\lambda(act)}} \quad [\text{eq. 10}]$$

where:

- $I_{0\lambda(xenon)}$ = photon flux (photons/cm²•day) over a 1 nm interval centered at wavelength λ
 j = conversion factor to make units consistent with the L/mol•cm unit of the molar absorption coefficient and the mol/L unit of concentration = 6.02 x 10²⁰ (L/cm³) (photons/mol)
 $k_{d\lambda(act)}$ = monochromatic direct photolysis rate constant (1/day, pseudo first-order) of an actinometer exposed to monochromatic irradiation at wavelength λ
 $\phi_{(act)}$ = the quantum yield of the actinometer
 ϵ_{λ} = molar absorption coefficient (L/mol•cm; M⁻¹•cm⁻¹) of the actinometer at wavelength λ
 D_{cell} = depth of irradiated cell (cm) = volume of irradiated cell/incident area
 I_{xenon} = light pathlength in cell exposed to a filtered xenon arc lamp

82. Equation 10 only gives the photon flux at one wavelength, but it can be used at different individual wavelengths wherever another monochromatic direct photolysis rate constant is determined for one or more low optical density actinometers. The determination of the photon flux at several different individual wavelengths spread throughout the wavelength range in which an estimate of the photon flux is desired should be sufficient to determine the photon flux from a filtered xenon arc lamp as a continuous function of wavelength. Because photon flux irradiation spectrum from a filtered xenon arc lamp is smooth, interpolation from known photon fluxes at several different wavelengths can be readily done (51).

83. By determining the polychromatic zero order direct photolysis rate constant for a high optical density actinometer of known quantum yield in PW in a photolysis cell irradiated with a filtered xenon arc lamp, the sum of the incident photon flux over the absorption spectrum of the actinometer above 295 nm can be determined from the following equation (51) (see Annex 4):

$$\sum_{\lambda=initial}^{\lambda=final} I_{0\lambda(xenon)} = \frac{j D_{cell}}{\phi_{act}} k_{d(act)(zero\ order)} \quad [\text{eq. 11}]$$

where:

- $(\lambda=initial)$ = initial wavelength of actinometer absorption (if ≥ 295 nm)
 $(\lambda=final)$ = final wavelength of the actinometer absorption (if ≤ 800 nm)
 $I_{0\lambda}$ = photon flux over a 1 nm interval centered at wavelength λ (photons/cm²•day)
 j = conversion factor to make units consistent with the L/mol•cm unit of the molar absorption coefficient and the mol/L unit of concentration = 6.02 x 10²⁰ (L/cm³)(photons/mol)
 $k_{d(act)(0\ order)}$ = monochromatic direct photolysis rate constant (zero order) of an actinometer exposed to monochromatic irradiation at wavelength λ (mol/L•day)
 D_{cell} = depth of irradiated cell (cm) = volume of irradiated cell/incident area (cm)
 ϕ_{act} = the quantum yield of the actinometer

85. By using more than one high optical density actinometer with absorption bands at different wavelengths, the sum of the photon flux over any desired range including the entire range between 295 and

800 nm can be determined. Further experimental details of procedures for determining the photon flux from and for calibrating xenon arc lamps are provided in references (37)(51).

Performance of direct photolysis study

Tier 1 - Theoretical screen.

86. For a test chemical which does not ionize significantly within a pH range of 5 to 9, a single UV-Visible absorption spectrum should be measured at a single pH within the 5 to 9 range where the hydrolysis rate, if any, is minimized. If the chemical is stable to abiotic hydrolysis, the spectrum should be measured at pH 7. The pH at which a direct photolysis study on a non-ionic test chemical is conducted should be the same as the pH at which the spectrum is determined. For a test chemical that is appreciably ionized anywhere within a 5 to 9 pH range, UV-Visible absorption spectra should be measured at pH 5, 7, and 9.

87. Electronic absorption spectra of the test chemical should be obtained in appropriate solvent systems at desired pHs with a spectrometer capable of recording UV-VISIBLE spectra between 295 and 800 nm. Because the higher energy (shorter wavelength) bands of many chemicals may sometimes tail into wavelengths above 295 nm, it is recommended that the spectrum be recorded 30 to 40 nm below 295 nm. The procedure to record, assign absorption band maxima, band-widths and determine decadic molar absorption coefficients has been described elsewhere (OECD Guideline 101). To obtain an adequate absorption spectrum, it may sometimes be necessary to enhance the solubility of the test chemical by using aqueous methanol, ethanol, or acetonitrile. It is recommended that UV-VISIBLE spectra of test chemicals be also obtained in the neat co-solvent.

88. If the test chemical absorbs above the 295 nm cutoff of solar irradiation at the earth's surface with $\epsilon_{\lambda} > 2 \text{ L/mol}\cdot\text{cm}$ ($\text{M}^{-1}\text{cm}^{-1}$) over at least 15 nm, estimate a maximum possible direct photolysis rate by assuming that the quantum yield is equal to one in equation 6 (2):

$$k_{d(\text{max})} = \sum_{\lambda=295}^{\lambda=800} \epsilon_{\lambda} L_{\lambda} \quad [\text{eq. 12}]$$

where:

- $k_{d(\text{max})}$ = maximum possible direct photolysis rate constant (1/day)
- ϵ_{λ} = molar absorption coefficient ($\text{L/mol}\cdot\text{cm}$; $\text{M}^{-1}\text{cm}^{-1}$) at wavelength λ
- L_{λ} = average daily solar photon flux ($\text{mmol photons/cm}^2\cdot\text{day}$) over wavelength interval centered at wavelength λ .

89. In estimating the maximum possible photolysis rate constant, the average daily solar photon fluxes L_{λ} substituted into equation 12 should be those for summer at 40° or 50° latitude. Values of L_{λ} can be readily obtained from tables (2)(12). As an alternative to the use of equation 12 and tables of L_{λ} , the maximum direct photolysis rate constant can be readily estimated by inputting molar absorption coefficients and a quantum yield equal to one into computer programs such as GCSOLAR (18) or ABIWAS (35)(36).

Criteria for deciding whether to go to Direct Photolysis Tier 2 or Tier 3

90. Determine if the maximum possible direct photolysis rate constant for the test chemical in the

near surface of a clear natural water exposed to an average daily solar photon flux would result in estimated direct photolysis losses $\geq 50\%$ of an initial concentration over 30 days/nights of sunlight exposure by substituting $k_{\max(\text{solar})}$ for $k_{(\text{solar})}$ in equation 9.

91. If estimated direct photolysis losses (assuming a maximum direct photolysis rate constant) are less than 50% of the initial concentration over a 30-day period direct photolysis is considered to be an insignificant process. In such a case, no further direct photolysis work is performed. If required, go to Indirect Photolysis Tier 1 (experimental/theoretical screen).

92. If estimated direct photolysis losses (assuming a maximum direct photolysis rate constant) are greater than or equal to 50% of the initial concentration over a 30-day period, go to Direct Photolysis Tier 2 (experimental screen and range finding) or Direct Photolysis Tier 3 (determination of the quantum yield).

Tier 2 - Experimental screen and range finding test for higher tiers

93. Dissolve the test chemical in sterilized, buffered pure water and place an optically dilute solution in photolysis test vessels. Expose at least half of the test vessels to a filtered xenon arc lamp or sunlight and allow an equal number or fewer of the test vessels to serve as dark controls.

94. Determine the concentrations of the test chemical in the irradiated test vessels and in the dark control test vessels at adequate enough sampling intervals to approximately determine the direct photolysis rate constant of the test chemical.

95. At each sampling interval, sacrifice an irradiated photolysis cell for analysis. The number of sampling intervals for which a dark control is also sacrificed for analysis should depend upon a prior knowledge of the rate of hydrolysis of the test chemical at the experimental pH. For example, if the test chemical is susceptible to appreciable rates of hydrolysis at the experimental pH, a dark control cell should be sacrificed for analysis each time an irradiated cell is sacrificed. However, if the test chemical is stable to hydrolysis at the experimental pH, a minimum of 3 sampling intervals for the dark control will be adequate.

96. If the data follow first-order kinetics, compute irradiated and dark control rate constants for the test chemical by using linear regression on equation 3 or non-linear regression on equation 2.

97. Once the irradiated and dark control rate constants for the test chemical have been determined, compute the approximate laboratory direct photolysis rate constant from the following equation:

$$k_{d(\text{screen})} = k_{\text{irradiated}} - k_{\text{dark}} \quad [\text{eq. 13}]$$

Estimation of direct photolysis rate constants in near surface clear natural water from laboratory values

98. Estimate a direct photolysis rate constant for the test chemical in near surface clear natural water exposed to average daily solar photon fluxes L_0 from the direct photolysis rate constant in a photolysis cell exposed to continuous photon fluxes from a filtered xenon arc lamp using the following equation (assuming D_{cell} the pathlength l ; see Annex 4):

$$k_{d(solar)} = \frac{j}{2.3} \frac{D_{cell}}{l} \frac{k_{d(xenon)} \sum_{295}^{800} \epsilon_{\lambda} L_{\lambda}}{\sum \epsilon_{\lambda} I_{0\lambda(xenon)}} \quad [\text{eq. 14}]$$

where:

- $k_{d(solar)}$ = average daily direct photolysis rate constant (1/day) for the test chemical in the near surface of clear natural water exposed to average daily solar irradiation fluxes L_{λ}
 $k_{d(xenon)}$ = direct photolysis rate constant (1/sec) for the test chemical in buffered pure water in photolysis cells exposed to constant filtered xenon arc lamp fluxes $I_{0\lambda}$
 $\epsilon_{\lambda(\text{chem})}$ = molar absorptivity of the test chemical (L/mol•cm; $M^{-1} \text{ cm}^{-1}$)
 D_{cell} = depth of irradiated cell (cm) = volume of irradiated cell/incident area (cm)
 l_{xenon} = light pathlength in cell exposed to a filtered xenon arc lamp
 $I_{0\lambda(xenon)}$ = incident filtered xenon arc lamp photon flux (photons/cm²•day) over a 1 nm interval centered at wavelength λ
 L_{λ} = 24 hour average daily solar photon flux over wavelength interval λ centered at wavelength λ for the weakly absorbing near surface of clear natural water bodies in (mmol photons/cm²•day)
 j = conversion factor = 6.02×10^{20} (L/cm³)(photons/mol)

99. To use equation 14, the photon flux from the filtered xenon arc lamp that is incident on the photolysis cells ($I_{0\lambda}$) must be determined as a function of wavelength using actinometers and (if available) a spectral radiometer. The solar photon fluxes as a function of wavelength for the near surface of clear natural waters (L_{λ}) for various mid-seasons and latitudes are readily available (2)(12).

Criteria for deciding whether to go to Direct Photolysis Tiers 3 and/or 4

100. Determine if the screen direct photolysis rate constant for the test chemical in the near surface of a clear natural water exposed to sunlight would result in estimated direct photolysis losses $\geq 20\%$ of an initial concentration over 30 days/nights of sunlight exposure by substituting $k_{d(\text{screen})(solar)}$ for $k_{d(solar)}$ in equation 9.

101. If estimated direct photolysis losses (assuming the screen direct photolysis rate constant) are less than 20% of the initial concentration over a 30-day light/dark sunlight exposure period, direct photolysis is considered to be an insignificant process. In such a case, no further direct photolysis work is performed. If required, proceed to the Indirect Photolysis Tier 1 screen.

102. If estimated direct photolysis losses (assuming the approximate direct photolysis rate constant) are greater than or equal to 20% of the initial concentration over a 30-day light/dark sunlight exposure period, proceed to Direct Photolysis Tiers 3 and/or 4. If determining the quantum yield of the test chemical and using it to estimate direct photolysis rate constants for types of water bodies, seasons, and latitudes is required, proceed to Direct Photolysis Tier 3. Otherwise, proceed to direct photolysis Tier 4 to perform a more definitive kinetics study.

Tier 3 - Determination of the quantum yield and estimations of direct photolysis rate constants

103. Determine the quantum yield of the test chemical in buffered solutions using monochromatic

irradiation (12), filtered xenon-arc lamp polychromatic irradiation (8) or sunlight polychromatic irradiation (2). Each has advantages and disadvantages compared to the others.

104. The main advantage in using monochromatic irradiation to determine the test chemical quantum yield of the test chemical is that (as will be shown later by equations 19 through 21) it eliminates the need to directly measure the incident monochromatic irradiation. However, a disadvantage is that it will take longer to determine the quantum yield with monochromatic irradiation than with the use of polychromatic irradiation because the actinometer and the test chemical are absorbing photon fluxes at just one wavelength instead of over multiple wavelengths.

105. The main advantage in using polychromatic irradiation (filtered xenon arc lamp or sunlight) instead of monochromatic irradiation to determine the test chemical quantum yield is that the time required to determine the quantum yield may be substantially shorter (8). The reason is due to the absorption of photon fluxes by the actinometer and test chemical over multiple wavelengths instead of just one wavelength. The main disadvantage in using polychromatic irradiation to determine the test chemical quantum yield is that unlike with monochromatic irradiation (as will be shown later by equations 20 and 21), its use requires the determination of the photon flux.

106. The advantage in using sunlight instead of a filtered xenon arc lamp, if polychromatic irradiation is used to determine the quantum yield, is that tables of average solar intensities as a function of season and latitude are readily available. Also, if sunlight is used, it eliminates the necessity of having a monochromatic or polychromatic artificial light source. However, if sunlight is used, an actinometer with an adjustable quantum yield is needed so the direct photolysis rate of the actinometer can be adjusted to be comparable to that of the test chemical under the same irradiation conditions (2)(12). Parallel exposure of the test chemical and actinometer to sunlight over comparable time frames minimizes errors due to changes in solar flux caused by fog, varying cloud cover, etc. (12)(51).

107. An example of an adjustable quantum yield actinometer is the p-nitroacetophenone - pyridine (PNAP-PYR) actinometer (52). For a 1.0×10^{-5} M p-nitroacetophenone solution, the quantum yield of the actinometer in experiments carried out with monochromatic irradiation at 313 nm can be adjusted by varying the concentration of pyridine in the solution according to the following equation (2)(12):

$$\phi_{act} = 0.0169 \cdot [\textit{pyridine}] \quad [\text{eq. 15}]$$

where:

ϕ_{act} = quantum yield of the 1.0×10^{-5} M p-nitroacetophenone

[pyridine] = molar concentration of pyridine

108. Suitable chemical actinometers used in aqueous photochemical studies include the following:

Actinometer System	Literature Citation
(a) p-nitroacetophenone/pyridine	52
(b) p-nitroanisole/pyridine	26, 52
(c) valerophenone	53
(d) ferrioxalate	19, 23, 37, 54, 55
(e) o-nitrobenzaldehyde	37, 52
(f) Reinecke's salt	12
(g) aberchrome 540	56, 57

109. The first two actinometers listed in the above table have adjustable quantum yields and are therefore particularly useful when solar irradiation is used (12). The first three actinometers listed in the table are low optical density actinometers and the last four are high optical density actinometers. The characteristics of those actinometers including the optimal wavelength range for their use are discussed in references 12 and 58. Other chemical actinometers are described in the IUPAC document on chemical actinometers (58).

Determination of the quantum yield using monochromatic irradiation

110. Place solutions of the test chemical and the selected optically low density actinometer in separate but identical photolysis cells. Irradiate at least half of the photolysis cells with monochromatic irradiation of wavelength λ and let an equal or fewer number (depending upon the hydrolytic stability of the test chemical) serve as dark controls. Determine the concentration of the test substance in the irradiated cells and in the dark controls at adequate enough sampling intervals to determine the monochromatic direct photolysis rate constant of the test chemical ($k_{d(\text{chem})}$) and of the actinometer ($k_{d\lambda(\text{act})}$) at the wavelength λ of irradiation. At each sampling interval, sacrifice an irradiated photolysis cell for analysis. The number of sampling intervals for which a dark control is also sacrificed for analysis should depend upon a prior knowledge of the rate of hydrolysis of the test chemical at the experimental pH.

11. The decline of a test chemical or actinometer concentrations at low optical density should follow pseudo first-order kinetics so that the monochromatic irradiated and the dark control rate constants can be determined by using linear regression on equation 3 or non-linear regression on equation 2. The decline of a test chemical or actinometer at high optical density should follow zero-order kinetics so that the monochromatic irradiated and the dark control rate constants can be determined by using linear regression on the following zero-order kinetics equation:

$$C = C_0 - kt \quad [\text{eq. 16}]$$

112. Once the monochromatic irradiated and dark control rate constants for the test chemical and the actinometer have been determined, the monochromatic direct photolysis rate constant of the test chemical ($k_{d(\text{chem})}$) and of the actinometer $k_{d\lambda(\text{act})}$ at wavelength λ are given by:

$$k_{d\lambda(\text{chem or act})} = k_{\lambda(\text{irradiated})(\text{chem or act})} - k_{\lambda(\text{dark})(\text{chem or act})} \quad [\text{eq. 17}]$$

Note: In a sterilized aqueous buffer, the dark control rate constant (k_{dark}) should be equal to the hydrolysis rate constant at the pH of the buffer.

113. Determine the molar absorption coefficients of the test chemical ($\epsilon_{\lambda(\text{chem})}$) and (if a low optical density actinometer is being used) the actinometer ($\epsilon_{\lambda(\text{act})}$) at the wavelength λ of the monochromatic irradiation using the Beer-Lambert law assuming that $\epsilon_{\lambda}C$ is \gg than the attenuation coefficient α_{λ} of the test medium:

$$\epsilon_{\lambda(\text{chem or act})} = \frac{A_{\lambda(\text{chem or act})}}{l[C_{(\text{chem or act})}]} \quad [\text{eq. 18}]$$

where:

- $\epsilon_{\lambda(\text{chem})}$ = molar absorption coefficient of the test chemical or actinometer
 L/mol•cm; $M^{-1}cm^{-1}$)
 $A_{\lambda(\text{chem or act})}$ = absorbance of test chemical or actinometer solution at wavelength λ
 L = light pathlength (cm) generally equivalent to D_{cell}
 $[C_{(\text{chem or act})}]$ = concentration of test chemical or actinometer solution (mol/L)

114. The quantum yield of an optically dilute test chemical determined using monochromatic irradiation and a low optical density (low absorbance) actinometer is given by (12)(47) (See Annex 4):

$$\phi_{\text{chem}} = \phi_{\text{act}} \frac{k_{d\lambda(\text{chem})} \epsilon_{\lambda(\text{act})}}{k_{d\lambda(\text{act})} \epsilon_{\lambda(\text{chem})}} \quad [\text{eq. 19}]$$

where:

- ϕ_{chem} = the quantum yield of the test chemical
 ϕ_{act} = the quantum yield of the actinometer
 $k_{d\lambda(\text{chem})}$ = monochromatic direct photolysis rate constant (1/day, pseudo first-order) of a test chemical exposed to monochromatic irradiation at wavelength λ
 $k_{d\lambda(\text{act})}$ = monochromatic direct photolysis rate constant (1/day, pseudo first-order) of an actinometer exposed to monochromatic irradiation at wavelength λ
 $\epsilon_{\lambda(\text{chem})}$ = molar absorption coefficient (L/mol•cm; $M^{-1}cm^{-1}$) of the test chemical at wavelength λ
 $\epsilon_{\lambda(\text{act})}$ = molar absorption coefficient (L/mol•cm; $M^{-1}cm^{-1}$) of the actinometer at wavelength λ

115. The quantum yield of an optically dilute test chemical determined using monochromatic irradiation and a high optical density (high absorbance) actinometer is given by (12)(47). See Annex 4:

$$\phi_{\text{chem}} = \frac{\phi_{\text{act}}}{2.3\epsilon_{\lambda(\text{chem})} D_{\text{cell}}} \frac{k_{d\lambda(\text{chem})}}{k_{d\lambda(\text{act})(\text{zero order})}} \quad [\text{eq. 20}]$$

where:

- ϕ_{chem} = the quantum yield of the test chemical
 ϕ_{act} = the quantum yield of the actinometer
 $k_{d\lambda(\text{chem})}$ = monochromatic direct photolysis rate constant (1/day, pseudo first-order) of a test chemical exposed to monochromatic irradiation at wavelength λ
 $k_{d\lambda(\text{act})(\text{zero})}$ = monochromatic direct photolysis rate constant (mol/L•day, zero-order) of an actinometer exposed to monochromatic irradiation at wavelength λ
 D_{cell} = depth of irradiated cell (cm) = volume of irradiated cell/incident area (cm)

116. The quantum yield of a test chemical at high optical density (high absorbance) determined using monochromatic irradiation and a high optical density (high absorbance) actinometer is given by (12)(47). See Annex 4):

$$\phi_{\text{chem}} = \phi_{\text{act}} \frac{k_{d\lambda(\text{chem})(\text{zero})}}{k_{d\lambda(\text{act})(\text{zero})}} \quad [\text{eq. 21}]$$

where:

- ϕ_{chem} = the quantum yield of the test chemical
- ϕ_{act} = the quantum yield of the actinometer
- $k_{d(chem)(zero)}$ = monochromatic direct photolysis rate constant (mol/L•day, zero-order) of a test chemical exposed to monochromatic irradiation at wavelength λ
- $k_{d(act)(zero)}$ = monochromatic direct photolysis rate constant (mol/L•day, zero-order) of an actinometer exposed to monochromatic irradiation at wavelength λ

117. As can be seen from equations 19, 20, and 21, it is not necessary to determine the photon flux if monochromatic irradiation is used to determine the test chemical quantum yield.

Determination of the quantum yield using polychromatic irradiation (lamp or sunlight)

118. The quantum yield of an optically dilute test chemical using a low optical density (low absorbance) actinometer and sunlight or a polychromatic filtered xenon arc lamp can be determined from equations 22 and 23, respectively (2)(6)(12)(See Annex 4):

$$\phi_{chem} = \phi_{act} \left(\frac{k_{d(chem)}}{k_{d(act)}} \right) \left(\frac{\sum_{\lambda=295nm}^{\lambda=800nm} \epsilon_{\lambda(act)} L_{\lambda}}{\sum_{\lambda=295nm}^{\lambda=800nm} \epsilon_{\lambda(chem)} L_{\lambda}} \right) \quad [\text{eq. 22}]$$

$$\phi_{chem} = \phi_{act} \left(\frac{k_{d(chem)}}{k_{d(act)}} \right) \left(\frac{\sum_{295}^{800} \epsilon_{\lambda(act)} I_{0\lambda(xenon)}}{\sum_{295}^{800} \epsilon_{\lambda(chem)} I_{0\lambda(xenon)}} \right) \quad [\text{eq. 23}]$$

where:

- $k_{d(chem)}$ = direct photolysis rate constant (1/day, pseudo first-order) of the test chemical
- $k_{d(act)}$ = direct photolysis rate constant (1/day, pseudo first-order) of the actinometer
- ϕ_{chem} = quantum yield of the test chemical (dimensionless ratio)
- ϕ_{act} = quantum yield of the actinometer (dimensionless ratio)
- $\epsilon_{\lambda(chem)}$ = molar absorption coefficient (L/mol•cm; $M^{-1} \text{ cm}^{-1}$) of the test chemical at wavelength λ
- $\epsilon_{\lambda(act)}$ = molar absorption coefficient (L/mol•cm; $M^{-1} \text{ cm}^{-1}$) of the actinometer at wavelength λ
- L_{λ} = average daily solar photon flux (mmol photons/cm²•day) over wavelength interval $\Delta\lambda$ centered at wavelength λ
- $I_{0\lambda(xenon)}$ = incident filtered xenon arc lamp photon flux (photons/cm²•day) over a 1 nm interval centered at wavelength λ

119. As can be seen from equations 22 and 23, it is necessary to independently and accurately determine the incident photon flux as a function of wavelength when polychromatic irradiation is used to determine the test chemical quantum yield.

120 The determination of the test chemical quantum yield using polychromatic irradiation and an actinometer are discussed in detail in (2) for the use of sunlight, and in (8) for the use of a filtered xenon arc lamp.

Dependence of the quantum yield on wavelength

121. Most of the direct photolysis equations involving polychromatic irradiation in this document and in the literature are presented with the quantum yield taken outside of the integral or summation over different wavelengths. The reason is that in aqueous solutions, the quantum yields of test chemicals are (in general) approximately independent of wavelength, even across different absorption bands. In aqueous solutions, molecules in higher excited electronic states tend to undergo radiationless decay to their first excited state before any photoreaction occurs (12). If photoreaction does occur, it generally occurs in competition with other deactivation processes while the molecule is in its first (not higher) excited electronic state.

122. However, the quantum yield may sometimes differ between absorption bands (6)(14). Therefore, it may sometimes be necessary to determine the quantum yield at least one wavelength for each adsorption band within the 295-800 nm range using monochromatic irradiation. The wavelength chosen for each absorption band should correspond to the maximum absorption. In cases where the quantum yield varies with wavelength, the quantum yield should be brought inside any integrals or summations over wavelengths.

123. In cases where the quantum yield remains constant within the same absorption band, but varies across different absorption bands, equations 5 and 6 for the direct photolysis rate constant can be modified to give:

$$k_d = \sum_{i=1}^{i=n} \phi_i \sum_{i\lambda(begin)}^{i\lambda(end)} \epsilon_{i\lambda} I_{0i\lambda} \quad [\text{eq. 24}]$$

$$k_d = \sum_{i=1}^{i=n} \phi_i \sum_{i\lambda(begin)}^{i\lambda(end)} \epsilon_{i\lambda} L_{i\lambda} \quad [\text{eq. 25}]$$

where:

- ϕ_i = quantum yield for absorption band i
- $\epsilon_{i\lambda}$ = molar absorption coefficient (L/mol•cm; $M^{-1} \text{ cm}^{-1}$) at wavelength λ within absorption band i
- $I_{0i\lambda}$ = photon flux per nm (photons/ $\text{cm}^2 \cdot \text{sec}/\text{nm}$) at wavelength λ within absorption band i
- λ_i = wavelength interval in nm generally = 1 nm
- $L_{i\lambda}$ = average daily solar photon flux irradiance (mmol photons/ $\text{cm}^2 \cdot \text{day}$) over wavelength interval $\Delta\lambda$ centered at wavelength λ within absorption band i
- I = indice for different absorption bands up to the maximum of n bands
- $i\lambda(\text{begin})$ = wavelength at the beginning of absorption band i
- $i\lambda(\text{end})$ = wavelength at the end of absorption band i

Use of the quantum yield to estimate direct photolysis rate constants

124. Once the quantum yield of a test chemical has been determined, it should be used as input into computer programs such as GCSOLAR (18) or ABIWAS (35)(36) to estimate direct photolysis rate constants for seasons, latitudes, and water body depths and light attenuations of interest. GCSOLAR and ABIWAS can be used to estimate direct photolysis rate constants at any given time in near surface water or at any specified depth. The programs can also average rate constants over any given time and/or depth interval of interest.

125. Although programs such as GCSOLAR or ABIWAS are readily available, equation 5 is often used to estimate the direct photolysis rate constant for optically dilute solutions of test chemicals in pure water in photolysis cells or in the near surface of clear natural water exposed to solar irradiation (2)(12).

Criteria for deciding whether to go to direct photolysis Tier 4

126. A Direct Photolysis Tier 4 kinetics study should be performed if identification/kinetics data on the major transformation products are applicable and if the direct photolysis rate constant(s) for the parent test chemical (estimated from its quantum yield) indicate that direct photolysis is a potentially significant process.

127. Determine if the direct photolysis rate constant (estimated from the quantum yield) for the test chemical in shallow natural water exposed to sunlight would result in estimated direct photolysis losses $\geq 20\%$ of an initial concentration over 30 days/nights of sunlight exposure by substituting $k_{d(\text{solar})}$ for $k_{(\text{solar})}$ in equation 9.

128. If estimated direct photolysis losses are less than 20% of the initial concentration over a 30 day light/dark sunlight exposure period, direct photolysis is considered to be an insignificant process. In such a case, no further direct photolysis work is performed. If of interest, proceed to indirect photolysis Tier 1. Proceed to direct photolysis Tier 4 if:

- Estimated direct photolysis losses are greater than or equal to 20% of the initial concentration over a 30 day light/dark sunlight exposure period, and
- The identification of major transformation products and/or the determination of their rates of formation and decline are required.

Tier 4 - Kinetics study on the test chemical and (if applicable) major transformation products

Experimental determinations of direct photolysis rate constants in the laboratory

129. In direct photolysis Tier 4, the decrease in the concentrations of the test chemical is determined in buffered pure water exposed to a filtered xenon arc lamp or sunlight. If applicable, the rates of formation and decline of major transformation products are also determined. For the purposes of this guideline, a major transformation product is one accounting for $\geq 10\%$ of the applied radioactivity (or molar basis) at any time during the study.

130. If a flow-through system is used to trap volatile test chemicals and/or their major transformation products, the following considerations should be made. The air should be passed through microbial filters to keep the samples sterile. Moist air should be used to prevent evaporation. The system should be checked for sterility at the study termination.

131. Place the test solution in photolysis test vessels. At least half the test vessels should be exposed

to a filtered xenon arc lamp or sunlight and an equal or fewer number of the test vessels should serve as dark controls.

132. Determine the concentrations in the irradiated test vessels and in the dark control test vessels at adequate enough sampling intervals to determine the direct photolysis rate constant of the test chemical.

133. At each sampling interval, sacrifice an irradiated photolysis cell for analysis. The number of sampling intervals for which a dark control is also sacrificed for analysis should depend upon the rate of hydrolysis of the test chemical at the experimental pH.

134. If the data follow first-order kinetics, compute irradiated and dark control rate constants for the test chemical by using linear regression on equation 3 or non-linear regression on equation 2.

135. Once the irradiated and dark control rate constants for the test chemical have been determined, compute the laboratory direct photolysis rate constant from the following equation:

$$k_d = k_{irradiated} - k_{dark} \quad [\text{eq. 26}]$$

136. If a filtered xenon arc lamp is used for irradiation, estimate an approximate average daily direct photolysis rate constant for the test chemical in shallow natural water exposed to average daily solar photon fluxes L_λ from equation 14.

137. In direct photolysis Tier 4, the decrease in the concentrations of the test chemical is determined in buffered pure water exposed to a filtered xenon arc lamp or sunlight. If applicable, the rates of formation and decline of major transformation products are also determined. For the purposes of this guideline, a major transformation product is one accounting for $\geq 10\%$ of the applied radioactivity at any time during the study.

138. If a flow-through system is used to trap volatile test chemicals and/or their major transformation products, the following considerations should be made. The air should be passed through microbial filters to keep the samples sterile. Moist air should be used to prevent evaporation. The system should be checked for sterility at the study termination.

139. The following equation can be used to estimate the direct photolysis rate constant for the test chemical in shallow natural water exposed to one or more different sunlight conditions from those in the study (see Annex 3 - Equation Derivations):

$$k_{(\text{sun shallow water})2} = k_{(\text{sun shallow water})1} \frac{\sum_{\lambda=295\text{nm}}^{\lambda=800\text{nm}} \epsilon_\lambda L_{\lambda(2)}}{\sum_{\lambda=295\text{nm}}^{\lambda=800\text{nm}} \epsilon_\lambda L_{\lambda(1)}} \quad [\text{eq. 27}]$$

where:

$k_{d(\text{sun shallow water})2}$ = estimated direct photolysis rate constant in the near surface of clear natural water exposed to solar irradiation fluxes ($L_{\lambda(2)}$) different from solar irradiation fluxes ($L_{\lambda(1)}$) used in the experiment.

$k_{d(\text{sun shallow water})1}$ = estimated direct photolysis rate constant in the near surface of clear natural water exposed to the experimental solar irradiation fluxes.

- $L_{\lambda(2)}$ = average daily solar photon fluxes different from those closest ($L_{\lambda(1)}$) to the experimental conditions.
- $L_{\lambda(1)}$ = average daily solar photon fluxes closest to the experimental ones based on the season and latitude at which the study was performed.

140. Compute direct photolysis half-lives by substituting the estimated direct photolysis rate constants into equation 4.

Major transformation products (if required)

141. Identify and quantify major phototransformation products using analytical methods and criteria indicated in paragraphs 39 through 43.

142. In cases where data follow first-order kinetics and the parent test chemical rapidly transforms, use the same first-order methods applied to the test chemical to also estimate first-order direct photolysis rate constants and corresponding half-lives for any major primary transformation products formed from the parent which are still at substantial concentrations (e.g. at $\geq 10\%$ of applied) after the parent has degraded to negligible levels.

143. Equation 14 for estimating sunlight rate constants from filtered xenon arc lamp rate constants and equation 27 for estimating a sunlight rate constant for a given season and latitude from a sunlight rate constant for a different season and/or latitude are also applicable to any first-order photolysis rate constants determined for any major transformation products.

144. In cases where primary or secondary transformation products are being substantially formed over the same time period they are being substantially lost, their direct photolysis rate constants and corresponding half-lives cannot be readily estimated as they were for the parent. However, as an option, attempts can be made to estimate first-order rate constants for the formation and decline of major transformation products using non-linear regression to fit concentration versus time series data to various equations derived from assumed transformation pathways.

Performance of indirect photolysis tiers

Tier 1 for indirect photolysis - Experimental and/or theoretical screen

145. Perform a screen in simulated water (containing humics as a surrogate for CDOM and when applicable, nitrate) or natural water to determine if indirect photolysis represents a potentially significant transformation pathway.

146. Place solutions of the test chemical in simulated natural water (SNW) and/or simulated natural water with nitrate (SHW-N) and/or natural water (NW) and in buffered pure water (PW) into equal numbers of photolysis cells. Expose at half of the photolysis cells containing each type of solution to sunlight and let an equal or smaller number of the photolysis cells containing each type of solution serve as dark controls.

147. The use of a filtered xenon arc lamp for indirect photolysis studies is not recommended at this time. The complexity of indirect photolysis processes does not allow straightforward extrapolation of results from filtered xenon arc lamps to sunlight equivalents and may not be feasible (2)(12).

148. Determine the concentrations in the irradiated photolysis cells and in the dark control photolysis cells at adequate enough sampling intervals to determine the irradiated and dark control rate constants of

the test chemical in SNW and/or SNW-N and/or in NW and in PW. At each sampling time, sacrifice an irradiated photolysis cell. The number of sampling intervals for which a dark control is also sacrificed for analysis should depend upon the stability of the test chemical in the dark control at the experimental pH. Assuming the decline of the test chemical follows first-order kinetics, determine the irradiated and dark control rate constants in the irradiated and dark control solutions by using linear regression on equation 3 or non-linear regression on equation 2.

149. Once the irradiated and dark control rate constants for the test chemical in SNW and/or SNW-N and/or NW and in PW have been determined, the net photolysis rate constants, the direct photolysis rate in PW, and the indirect photolysis rates constants can be respectively determined from the following equations:

$$k_{pX} = k_{X(irrad)} - k_{X(dark)} \quad [\text{eq. 28}]$$

$$k_{d(PW)} = k_{PW(irrad)} - k_{PW(dark)} \quad [\text{eq. 29}]$$

$$k_{iX(\text{approx})} = k_{pX} - k_{d(PW)} \quad [\text{eq. 30}]$$

where:

X = SNW, SNW-N, or NW

Note: Equation 30 is only approximate because the direct photolysis rate constant in PW ($k_{d(PW)}$) will be greater than the direct photolysis rate constant in SNW, SNW-N or NW (k_{dX}) due to light attenuation (12). However, the approximation is adequate for a screen. Also, unlike indirect photolysis Tier 2, this indirect photolysis Tier 1 screen does not take into account the photobleaching of humic solutions in photolysis cells by sunlight as reported by Winterle and Mill (59).

150. Determine if the approximate indirect photolysis rate constant for the test chemical in shallow natural surface water would result in estimated indirect photolysis losses $\geq 20\%$ of an initial concentration over 30 days/nights of sunlight exposure by substituting $k_{iX(\text{approx})}$ for $k_{(\text{solar})}$ in equation 9.

151. If estimated indirect photolysis losses (assuming an approximate indirect photolysis rate constant) are less than 20% of the initial concentration over a 30 day/night sunlight exposure period, indirect photolysis is considered to be an insignificant process. In such a case, no further indirect photolysis work is performed.

152. If estimated indirect photolysis losses (assuming an approximate indirect photolysis rate constant) are greater than or equal to 20% of the initial concentration over a 30-day light/dark sunlight exposure period, indirect photolysis is considered to be a potentially significant process. Proceed to Indirect Photolysis Tier 2 to perform a more definitive kinetics study.

153. Mill (21) has summarized structural activity relations (SARs) for estimating second-order rate constants for the reaction of organics with photooxidants in water. He also summarized typical concentrations of various photooxidants generally found in the top layers of surface water exposed to sunlight. In some cases, it may be possible to supplement or even replace the experimental screen with a theoretical screen based on using structural activity relationships (SARs). These SARs estimate rate constants and information on the typical concentrations of photooxidants in surface water. Although a theoretical screen involving one or two potential photooxidants may indicate that going to Tier 2 is justified, it is doubtful that one can indicate that going to Tier 2 is not justified. The reason is that a

theoretical screen will generally cover only one or two of the large number of possible types of indirect photolysis reactions. Further details on using structure activity relations for estimating rate constants for the reaction of test chemicals with photooxidants in water such as the hydroxyl radical and singlet oxygen are provided in reference 51.

Tier 2 - Experimental determination of rate constants (and identification/quantification of major transformation products, when required)

154. In the indirect photolysis Tier 2, the decrease in the concentration of the test chemical is determined in simulated natural water (SNW) and/or simulated natural water with nitrate (SNW-N) and/or one or more natural surface waters (NW) and in buffered pure water (PW) exposed to sunlight. If applicable, the identities and rates of formation and decline of major transformation products are also determined. For the purposes of this guideline, a major transformation product is one accounting for $\geq 10\%$ of applied at any time during the study.

155. The performance of Tier 2 differs from that in Tier 1 in several ways including:

- The number of sampling times is greater.
- The direct photolysis constant in humic water is estimated by inputting the chemical's quantum yield and the attenuation constants of the humic solution into GCSOLAR or ABIWAS.
- If applicable, the rates of formation and decline of major transformation products are determined.
- If a study lasts for several days or more such that "photobleaching" of the humic solutions in photolysis cells may be substantial in some cases, it can (as an option) be accounted for as indicated in Leifer (12) and OPPTS 835.5270(2).

156. Dissolve the test chemical in SNW and/or SNW-N and/or NW and in PW and place the solutions in equal numbers of photolysis cells. Expose at least half of the photolysis cells containing each type of solution to sunlight and let an equal or lesser number of the photolysis cells containing each type of solution serve as dark controls.

157. Determine the concentrations in the irradiated cells and in the dark controls at adequate enough sampling intervals to determine the irradiated and dark control rate constants of the test chemical in simulated natural water (SNW), and/or simulated natural water with nitrate (SNW-N), and/or natural surface water (NW), and in buffered pure water (PW). At each sampling interval, sacrifice an irradiated test vessel for analysis. Sacrifice dark controls for analysis at an equal or fewer number of sampling intervals

158. Determine the irradiated and dark control rate constants of the test chemical in SNW and/or SNW-N and/or NW and in PW by using linear regression on equation 3 or non-linear regression on equation 2.

159. Once the irradiated and dark control rate constants for the test chemical in SNW and/or SNW-N and/or NW and in PW have been determined, the net photolysis rate constants in those waters and the direct photolysis rate constants in PW can be determined from equations 28 and 29.

160. If the same light source and photon flux, test vessels, and experimental set-up are used for the definitive determination of the direct photolysis rate constant in PW in the Tier 4 Direct Photolysis study, a separate determination of the direct photolysis rate constant in PW in the Tier 2 Indirect Photolysis study as just described is not necessary.

Determination of direct photolysis rate constant in SNW, and/or SNWN, and/or NW from one in PW

161. Determine attenuation constants as a function of wavelength for all experimental waters (SNW, SNW-N, and/or NW and PW) from the following equation:

$$\alpha(\lambda) = \frac{A(\lambda)}{l} \quad [\text{eq. 31}]$$

where:

$\alpha(\lambda)$ = light attenuation constant as a function of wavelength λ (1/cm)
 $A(\lambda)$ = absorbance of test medium as a function of wavelength λ
 l = light pathlength in cell (cm)

162. Estimate average daily direct photolysis rate constant for the test chemical in near surface PW and in SNW and/or SNW-N, and/or NW by inputting its quantum yield and attenuation constants for PW and for SNW, and/or SNW-N, and/or NW into GCSOLAR or ABIWAS. If the quantum yield of the test chemical was determined in Direct Photolysis Tier 3, use it as input. Otherwise, estimate the quantum yield by substituting the experimental direct photolysis rate constant in PW and $\epsilon_{\lambda}L_{\lambda}$ into equation 6 and rearranging to solve for the quantum yield.

163. Estimate the direct photolysis rate constant in SNW and/or SNWN and/or NW in a photolysis cell from the following equation:

$$k_{dX} = \frac{\overline{k_{dX} \text{ (GCSOLARorABIWAS)}}}{k_{d(PW) \text{ (GCSOLARorABIWAS)}}} k_{d(PW)(\text{exp})} \quad [\text{eq. 31}]$$

where:

X = SNW, SNW-N, or NW

k_{dX} = direct photolysis rate constant in SNW, SNWN, or NW in a photolysis cell

$k_{dX(\text{GCSOLAR})}$ = GCSOLAR or ABIWAS estimated average daily direct photolysis rate constant in near surface SNW, SNW-N, or NW

$k_{d(PW)(\text{GCSOLAR})}$ = GCSOLAR or ABIWAS estimated average daily direct photolysis rate constant in PW

$k_{d(PW)(\text{exp})}$ = experimentally determined direct photolysis rate constant in PW in a photolysis cell

164. Once the net and direct photolysis rate constants in SNW and/or SNW-N and/or NW have been determined, the indirect photolysis rate constant in those waters can be estimated from the following equation:

$$k_{iX} = k_{pX} - k_{dX} \quad [\text{eq. 32}]$$

where X = SNW, SNW-N, or NW

165. The methods used in the identification and kinetics analysis of transformation products formed during indirect photolysis studies are comparable to those formed during direct photolysis studies.

Method of accounting for “photobleaching”

166. If a study lasts for several days or more, the decline of the test chemical in irradiated SNW, SNW-N, or NW may not be first-order due to the “photobleaching” of humic solutions. Photobleaching in photolysis cells that has been studied and reported by Winterle and Mill (54).

167. Photobleaching does not appear to be a significant process in the actual environment because CDOM appears to be generated at much faster rates than the rates of its decline through photobleaching (51). However in the laboratory, the photobleaching of humic solutions in photolysis cells by sunlight somewhat complicates a more definitive determination of the indirect photolysis rate. Because of photobleaching, the indirect photolysis rate constant for a test chemical in SNW, SNW-N, or NW solutions in photolysis cells exposed to sunlight decreases over time. If that occurs, there are two options:

168. When photobleaching begins to become substantial, the study can be terminated. In such cases, only data obtained from the study prior to substantial photobleaching should be used in the analysis. The study can be continued by accounting for photobleaching.

Extrapolation from cell or near surface to the same water over a deeper depth, and from experimental to other solar photon fluxes

169. Unfortunately, methods of extrapolation to greater depths and light attenuation and to other solar conditions are not as straightforward for indirect photolysis as they are for direct photolysis, even when irradiation is restricted to sunlight. The reason is that indirect photolysis may involve the absorption of solar flux by many different types of sensitizers with different absorption spectra and by nitrate. Therefore, the results of an indirect photolysis study conducted in cells exposed to natural sunlight are only applicable to the near surface and the same set of solar conditions as the experimental ones.

REPORTING OF DATA AND RESULTS

170. The degree of presentation of results depends on the complexity and purpose of the study, that is, the number of tiers.

Direct photolysis data and results

Tier 1

- Provide the UV-VISIBLE spectrum or spectra of the test chemical as the molar absorption coefficients ($L/mol \cdot cm$ or $M^{-1}cm^{-1}$) on the y-axis versus wavelengths (nm) on the x-axis.
- Report the estimated maximum photolysis rate constant and associated direct photolysis losses over a 30 days/nights sunlight exposure period. Provide the equations and calculations used to estimate them. Provide the rationale for selecting the season and latitude of the average daily solar photon fluxes (L_{λ}) used in the calculations. Report whether or not the results of the calculations trigger Direct Photolysis Tiers 2 and/or 3.

Tier 2

- If a filtered xenon arc lamp was used, provide the incident photon flux in a graph as the photon flux ($photons/cm^2 \cdot sec$) on the y-axis versus the wavelength (nm) on the x-axis.

- If sunlight was used, provide tabular values of solar photon fluxes for the season and latitude closest to those of the study.
- Provide table(s) and graph(s) which show the concentrations of the test chemical in irradiated and dark control solutions versus time. Show the best fit regression lines on the graph(s) along with the data points.
- Report the irradiated, dark control, and approximate direct photolysis rate constant of the test chemical along with their corresponding half-lives. Provide the equations, calculations, and regression coefficients used to compute them together with regression n and r^2 values, and standard errors of coefficients (for example, slope, intercept).
- Based upon the approximate direct photolysis rate constant, report the associated estimated direct photolysis losses over a 30 days/nights sunlight exposure period. Provide the equations and calculations used to estimate them. Provide the rationale for selecting the season and latitude of the average daily solar photon fluxes (L_λ) used in the calculations. Report whether or not the results of the calculations trigger Direct Photolysis Tiers 3 and/or 4.

Tier 3

- For the determination of the test chemical quantum yield with the use of an actinometer, provide table(s) and graph(s) showing the concentrations of the test chemical and actinometer in irradiated and dark control solutions versus time. Show the best fit regression lines on the graph(s) along with the data points.
- Report the irradiated, dark control, and direct photolysis rate constants of the test chemical and actinometer. Provide the equations, calculations, and regression coefficients used to compute them together with regression n and r^2 values, and standard errors of coefficients (for example, slope, intercept).
- Report the quantum yield of the test chemical. Provide the equation and calculation used to compute it.
- Report estimated direct photolysis rate constants for the test chemical in natural water that are estimated from the test chemical quantum yield for seasons, latitudes, and water body types of interest. Provide and/or describe the equations and calculations or computer program (e.g. GCSOLAR or ABIWAS) and inputs to estimate them.

Tier 4

- If a filtered xenon arc lamp was used, provide the incident photon flux in a graph as the photon flux (photons/cm²•sec) on the y-axis versus the wavelength (nm) on the x-axis.
- If sunlight was used, provide tabular values of solar photon fluxes for the season and latitude closest to those of the study.
- Provide table(s) and graph(s) showing the concentrations of the test chemical and (if applicable) major phototransformation product concentrations and mass balance determinations in irradiated and dark control solutions versus time. Show the best fit regression lines on the graphs along with the data points.

- Report the irradiated, dark control, and direct photolysis rate constants of the test chemical along with their corresponding half-lives. Provide the equations, calculations, and regression coefficients used to compute them together with regression n and r^2 values, and standard errors of coefficients.
- If applicable, report the rate constants for the formation and decline of the major transformation products. Provide the transformation pathway model (see next paragraph), equations, calculations, and regression coefficients used to compute them together with regression n and r^2 values, and standard errors of coefficients.
- Provide chemical structures and names of the test chemical and (if applicable) major transformation products in both irradiated and dark control solutions. Provide graphical presentations of postulated transformation pathways in both the irradiated and dark control solutions.

Indirect photolysis data and results

Tier 1

- Assuming sunlight was used for indirect photolysis as recommended, provide tabular values of solar photon fluxes for the season and latitude closest to those of the study.
- Provide important characteristics of all simulated and/or natural waters used including DOC, humic content (if simulated), pH, dissolved oxygen, nitrate. Include the UV-VISIBLE spectrum of the test media from 295 to 800 nm. For natural water, include site of collection.
- Provide table(s) and graph(s) showing the concentrations of the test chemical in irradiated and dark control solutions versus time. Show the best fit regression lines on the graph(s) along with the data points.
- Report the irradiated, dark control, and approximate net, direct, and indirect photolysis rate constants of the test chemical along with their corresponding half-lives.. Provide the equations, calculations, and regression coefficients used to compute them together with regression n and r^2 values, and standard errors of coefficients.
- Report the approximate indirect (or indirect plus hydroxyl) photolysis rate constant and associated indirect photolysis losses over a 30 days/nights sunlight exposure period. Provide the equations and calculations used to estimate them. Provide the rationale for selecting the season and latitude of the average daily solar photon fluxes (L_λ) used in the calculations. Report whether or not the results of the calculations trigger Tier 2 Indirect Photolysis.

Tier 2

- Provide tabular values of solar photon fluxes for the season and latitude closest to those of the study.
- Provide important characteristics of all simulated and/or natural waters used including DOC, humic content (if simulated), pH, dissolved oxygen, and nitrate. The UV-VISIBLE spectrum (295 to 800 nm) of the test media should be included. For natural water, include the site of collection.
- Provide table(s) and graph(s) showing the concentrations of the test chemical and (if applicable) major transformation product concentrations and mass balance determinations in irradiated and dark control

solutions versus time. Show the best fit regression lines on the graphs along with the data points.

- Report the irradiated, dark control, and net, direct, and indirect photolysis rate constants of the test chemical along with their corresponding half-lives. Provide the equations, calculations, and regression coefficients used to compute them together with regression n and r^2 values, and standard errors of coefficients. If applicable and possible, supply the same information for major transformation products.
- If applicable, report the rate constants for the formation and decline of the major transformation products. Provide the transformation pathway model (see next paragraph), equations, calculations, and regression coefficients used to compute them together with regression n and r^2 values, and standard errors of coefficients.
- Provide chemical structures and names of the test chemical and (if applicable) major transformation products in both irradiated and dark control solutions. Provide graphical presentations of postulated transformation pathways in both the irradiated and dark control solutions.

Additional reporting requirements

General information

- Title of the study, author(s), performing laboratory (name and address), laboratory report identification number, date of completion. In some instances, it may be necessary to identify who is submitting the study, their address and any other identification number.
- Name(s) of the test substance, chemical nomenclature, Chemical Abstracts Registry Number (CAS Reg. No.). A tabular format may be used to present this information, but it is optional.
- Physical and chemical properties applicable to the test substance. As an option, these physical and chemical properties may be listed in a table.
- Report if the test substance is the primary chemical or any transformation product resulting from abiotic hydrolysis and/or biotransformation. Report if the test substance is an industrial chemical, a pharmaceutical chemical, a pesticide, etc.
- For radiolabelled test substances, the radiolabelled element and isotope, radiolabelling position(s), chemical and radiolabel purity, and specific activity should be reported.

Experimental information

- Standard laboratory equipment and reagents.
- Analytical method(s) used for identifying and quantifying the test substance. The report should include a brief description of the method, reference standards, instrumentation, accuracy and precision, LOD and LOQ. Results of independent laboratory validation (if required).
- Quality Control (QC) results such as analytical recoveries and relative percent standard deviations for replicate analyses.

Specific experimental information related to photolysis (60)

- Experimental conditions, reagents, reaction vessels and other information relevant to each of the tiers comprising the study. This may include:
 - Temperature
 - Solvent and/or buffers used for preparing stock and test solutions for direct photolysis, including dark control samples.
 - Co-solvent and percent by volume used, if any.
 - Nominal and actual concentration of test substance in the test media
- Absorption Spectroscopy:
 - Description of instrumentation
 - Pathlength and material of optical cells
 - Spectral resolution
 - Concentration of test chemical in solution
 - Co-solvent and percent by volume used, if any
 - Temperature and pH
- Specific information on reaction vessels:
 - Material (type of glass, quartz, etc)
 - Geometry of the reaction vessels and positioning of the reaction vessels with respect to the light source.
 - Any significant optical properties of the vessel material (wavelength cut-off, etc.)
 - Illustration of the reaction vessel(s) arrangement and/or a photograph is encouraged to be included in the report.
- Xenon-light source:
 - Manufacturer, model
 - Filters and their purpose
 - Measured spectrum of the light source between 295 and 800 nm at at least the beginning and end of the study.
 - Comparison of the spectrum of the light with that of natural sunlight for the conditions required for specific tiers.
 - Intensity (radiant flux, fluence rate) at sample ($\text{J m}^{-2}\text{s}^{-1}$; photons $\text{m}^{-2}\text{s}^{-1}$) and area irradiated.
- Irradiation dose (fluence) (J m^{-2}):
 - State if continuous or intermittent irradiation was used
 - If continuous irradiation, state radiant flux (intensity) and time
 - If intermittent irradiation, state radiant flux, cycle duration and number of cycles
- Quantum Yields:
 - Experimental conditions (temperature, test media, concentration of test substance in test media)
 - Description of reaction vessels (diagram and/or photograph)
 - Specify if monochromatic or polychromatic irradiation was used and source

- Monochromatic wavelength and bandwidth used.
 - Intensity (radiance flux)
 - Photometric methods, if any
 - Chemical actinometer used (criteria for selection, concentration of actinometer in test media, absorption spectrum of the actinometer in the test media).
 - Positioning of the actinometer with respect to the test substance
- Computational methods for:
 - Calculation of molar absorption coefficients (ϵ_λ) utilizing Beer-Lambert's relationship
 - Maximum photolysis reaction rate assuming $\phi = 1$ (direct and/or indirect photolysis)
 - Experimental photolysis reaction rate (direct and/or indirect photolysis)
 - Quantum yield calculations (quantum yield should be expressed as a fraction and not as a percent)
 - GCSOLAR or ABIWAS calculation of reaction rates at different latitudes, seasons, time of the day, water bodies.
 - Half-lives or DT_{50} , DT_{75} , and DT_{90} values and appropriate associated confidence intervals.

Discussion

171. The purpose of conducting the study should be discussed in terms of the potential for the test chemical to be present in surface water. For example, chemicals can be transported to surface water in numerous ways including by direct point discharge into water bodies, runoff, spray drift or atmospheric deposition.

172. The depth of the discussion depends on the complexity of the study. Regardless of the complexity of the study, the discussion should be focused on the effect sunlight may have on the rate and pathway of transformation of the test chemical in aqueous environments.

173. The potential for the test chemical to undergo direct and/or indirect photolysis should be discussed. When applicable, the rate constants for irradiated and dark control test chemical should be compared to distinguish between hydrolytic and photolytic transformations. When possible, discuss the relative contribution(s) of direct and indirect photolysis to the overall net photolysis rate.

174. When quantum yields are determined, the calculated rate constants at different latitudes, seasons and for water bodies with depths and light attenuation coefficients of interest should be used to discuss how sunlight would affect the transformation rate of the test chemical at the time when the concentration of the chemical in surface water is expected to be the maximum.

175. When transformation products are identified and quantified in direct and indirect photolysis studies, photolytic products should be distinguished from hydrolytic products. When feasible, potential hydrolytic and/or photolytic stability of primary transformation products should be included in the results. When available, the rates of formation and decline of primary transformation products should be discussed. In turn, transformation products from direct and indirect photolysis studies should be compared to distinguish products unique to each.

176. When studies are conducted with both SNW and SNW-N, the potential contribution of hydroxyl radical should be assessed by comparing the results in the two types of water.

177. Sources of error and uncertainty such as losses of the test chemical and/or transformation products due to volatilization and/or adsorption to glassware should be discussed.

LITERATURE

1. OECD. 1998. OECD Working Group for the Development of a Test Guideline on Phototransformation of Chemicals in Water. Rome, 21- 22 September 1998.
2. U.S. EPA. 1998. OPPTS 835.2210 - Direct Photolysis Rate in Water by Sunlight. United States Environmental Protection Agency. Washington, DC.
http://www.epa.gov/docs/OPPTS_Harmonized/835_Fate_Transport_Transformation_Test_Guidelines/Series/
3. U.S. EPA. 1998. OPPTS 835.5270 - Indirect Photolysis Screening Test. United States Environmental Protection Agency. Washington, DC.
4. ASTM. 1987. E 896-87: Standard Test Method for Conducting Aqueous Direct Photolysis Tests. American Society for Testing and Materials. Philadelphia PA.
5. U.K. DOE. 1993. Determination of the Stability of Substance in Simulated Sunlight- A proposal for a Test Guideline. Submitted by the Department of the Environment, United Kingdom.
6. UBA. 1992. Direct Phototransformation of Chemicals in Water - A proposal for a Test Guideline. Submitted by UBA, Germany. Berlin.
7. SETAC. 1995. Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides. Section 10 in Aqueous Photolysis (page 28- 30). Mark Lynch, Editor. SETAC - Europe Publication.
8. ECETOC. 1984. The Phototransformation of Chemicals in Water: Results of a Ring Test. ECETOC Technical Report N° 12. Brussels, Belgium
9. Van Henegouven B. 1990. Sunlight induced Degradation of Chemicals in Surface Water. Report of Centre for Bio-Pharmaceutical Sciences. Leiden, The Netherlands.
10. OECD. 1997. Guidance Document on Direct Phototransformation of Chemicals in Water. OECD Environmental Health and Safety Publication. Series on Testing and Assessment No.7. Paris, France.
11. IUPAC. 1996. Glossary of terms used in photochemistry (IUPAC Recommendations 1996) Pure & Appl. Chem. 68: pp 2223 - 2286.
12. Leifer A. 1988. The Kinetics of Environmental Aquatic Photochemistry. Theory and Practice. ACS Professional Reference Book. Published by the American Chemical Society. Washington, D.C.
13. Mill T and Mabey W. 1985. Photodegradation in water. Chapter 8 in Environmental Exposure from Chemicals. Neely W and Blau G, editors. CRC Press. Boca Raton FL. pp. 175-216
14. Harris J. 1982. Rates of Direct Aqueous Photolysis. Chapter — in Handbook of Chemical Property Estimation Methods. Environmental Behavior of Organic Compounds. Lyman W, Reehl W, and Rosenblatt D, editors. McGraw-Hill Publishers. New York, NY.

15. Mill T, Mabey W, Bomberger D, Chou T, Henry D, and Smith JH. 1982. Laboratory Protocols for Evaluation of the Fate of Organic Chemicals in Air and Water. U.S. Environmental Protection Agency. EPA 600/3-82-002. Washington, D.C.
16. Mill T, Davenport J, Dulin D, Mabey W, and Bawol R. 1981. Evaluation and Optimization of Photolysis Screens. U.S. Environmental Protection Agency. EPA 560/5-81-003. Washington, D.C.
17. Zepp R. 1978. Quantum yields for reaction of pollutants in dilute aqueous solutions. *Environ. Sci. & Technol.* 12: pp. 327-329.
18. Zepp R, and Cline D. 1977. Rate of direct photolysis in aquatic environment. *Environ. Sci. & Technol.* 11(4): pp. 359-366.
19. Zepp R, Schlotzhauer P, and Sink R. 1985. Photosensitized transformations involving electronic energy transfer in natural waters: Role of humic substances. *Environ. Sci. & Technol.* 19: pp. 74-81.
20. Zepp R, Baughman G, and Schlotzhauer P. 1981. Comparison of photochemical behavior of various humic substances in Water. I. Sunlight induced reactions of aquatic pollutants photosensitized by humic substances. *Chemosphere* 10: pp. 109-117.
21. Mill T. 1999. Predicting photoreaction rates in surface water. *Chemosphere* 38(6): pp. 1379-1390.
22. Brezonik P and Fulkerson-Brekken J. 1998. Nitrate-induced photolysis in natural waters: Controls on concentrations of hydroxy radical photo-intermediates by natural scavenging agents. *Environ. Sci. & Technol.* 32: 3004-3010.
23. Vaughan P and Bough N. 1998. Photochemical formation of hydroxy radical by constituents of natural waters. *Environ. Sci. Technol.* 32: 2947-2953.
24. Blough N and Zepp R. 1995. Reactive oxygen species in natural waters. Chapter in *Active Oxygen in Chemistry*. Foote C, Valentine G, Greenberg A, and Liebman J, editors. Published by Chapman and Hall. New York, NY. pp. 280-333.
25. Mabury S and Crosby D. 1994. The relationship of the hydroxyl reactivity to pesticide persistence. Chapter 10 in *Aquatic and Surface Photochemistry*. G Helz, R Zepp, and D Crosby, editors. Lewis Publishers. Boca Raton, Florida, USA. pp. 149- 161.
26. Zepp, R.G., Hoigne, J. and Bader, H. 1987. Nitrate-induced photooxidation of trace organics in water. *Environ. Sci. Technol.* 21: 443-450.
27. Haag W and Hoigne' J. 1986. Singlet oxygen in surface waters. III. Steady state concentrations in various types of waters. *Environ. Sci. & Technol.* 20: 341-348.
28. Haag W, Hoigne' J, Gassmann E, and Braun A. 1984. Singlet oxygen in surface waters. II. Quantum yields of its production by some natural humic materials as a function of wavelength. *Chemosphere* 13: pp. 641-650.

29. Mill T, Hendry D, and Richardson H. 1980. Free radical oxidants in natural waters. *Science* 207: pp. 886-889.
30. Draper W and Crosby D. 1981. Hydrogen peroxide and hydroxyl radical: Intermediates in indirect photolysis reactions in water. *J. Agric. Food Chem.* 29: pp. 699.
31. Wolff C, Halmans M and Van der Heijde H. 1981. The formation of singlet oxygen in surface waters. *Chemosphere* 10: pp. 59.
32. Zepp R, Wolfe N, Baughman G, and Hollis R. 1977. Singlet oxygen in natural waters. *Nature* 267: pp. 421-423.
33. Zhou, X. and Mopper, R. 1990. Determination of photochemically produced hydroxyl radicals in seawater and fresh water. *Mar. Chem.* 30: 71-88.
34. Mopper, R. and Zhou, X. 1990. Hydroxyl radical photoproduction in the sea and its potential impact in marine processes. *Science* 250: 661-664.
35. Frank R and Klöpffer W. 1988. Spectral solar photo irradiance in Central Europe and the adjacent North Sea. *Chemosphere* 10: p. 985.
36. Frank R and Klöpffer W. 1988. A convenient model and program for the assessment of abiotic degradation of chemicals in natural waters. *Ecotox. Environ. Safety* 17: pp. 323-332.
37. Calvert, J.G. and Pitts, J.N., Jr. 1966. *Photochemistry*. Wiley, New York, USA.
38. Turro N. 1991. *Modern Molecular Photochemistry*. Published by University Science Books. Sausalito, California, USA.
39. Zepp R. 1999. Personal communication (December 30, 1999).
40. Faust B. 1994. A review of the photochemical redox reactions of iron(III) species in atmospheric, oceanic, and surface waters: Influence on geochemical cycles and oxidant formation. Chapter 1 in *Aquatic and Surface Photochemistry*. G Helz, R Zepp, and D Crosby, editors. Lewis Publishers. Boca Raton, Florida, USA. pp. 3- 35
41. Suizberger B, Laubscher H, and Karametaxas G. 1994. Photoredox reactions at the surface of iron (III) hydr(oxides). Chapter 3 in *Aquatic and Surface Photochemistry*. G Helz, R Zepp, and D Crosby, editors. Lewis Publishers. Boca Raton, Florida, USA. pp. 53- 73.
42. U.S. EPA. 1985. Hazard Evaluation Division. Standard Evaluation Procedure: Aqueous Photolysis Studies. Office of Pesticide Programs, U.S. Environmental Protection Agency. EPA-540/9-85-014
43. Ruzo L, Shepler K, and Toia R. 1995. Pesticide hydrolysis and photolysis studies: Guideline challenges and experimental approaches. Chapter 8 in *Agrochemical Environmental Fate - State of the Art*. M Leng, E Leovey, and P Zubkoff, editors. Lewis Publishers. Boca Raton, Florida, USA. pp 77- 91.

44. Gao H and Zepp R. 1998. Factors influencing photoreactions of dissolved organic matter in a coastal area of the Southeastern United States. *Environ. Sci. Technol.* 32: 2940-2946.
45. IHSS. 1999. Typical Humic Acid Data Packet. International Humic Substances Society (IHSS). Available from website <http://ihss.gatech.edu/dataaha.html>.
46. Zepp R and Schlotzhauer P. 1981. *Chemosphere* 10: pp. 479
47. Zepp, R.G. 1982. Experimental Approaches to Environmental Photochemistry. Chapter in the Handbook of Environmental Photochemistry, edited by Hutzinger, O.; Springer-Verlag, New York 2, Part B: pp 19-40.
48. Faust, B.C. 1993. Generation and use of simulated sunlight in photochemical studies of liquid solutions. *Rev. Sci. Instrum.* 64:(2) pp. 577- 578.
49. (a) The Book of Photon Tools. 1999. Drozdowicz, Z., Editor. Oriel Instruments, Stratford, Connecticut 006615, USA. (b) Atlas Electric Devices Company, 114 Ravenswood Avenue, Chicago, Illinois 60613 USA. Oriel Instruments. 1999.
50. Lemarie, J., Guth, J. A., Klais, D., Leahey, J., Merz, W., Philp, J. Wilmes, R., and Wolff C.J.M. 1985. *Chemosphere*, 14: pp 53- 77.
51. Mill T. 2000. Documents on Calibration of Lamp and Indirect Photoreaction Estimation Methods, prepared for and submitted to the U.S. Environmental Protection Agency, Office of Pesticide Programs under PR Number 9W-2901-NASA, February 22, 2000.
52. Dulin D. and Mill T. 1982. Development and evaluation of sunlight actinometers. *Environ. Sci. Technol.* 16(11): pp. 815-820.
53. Zepp, R.G., Gumz, M.M., Miller, W., and Gao, H. 1998. Photoreaction of Valerophenone in Aqueous Solutions. *J. Phys. Chem. A*, 102: pp. 5716- 5722.
54. Murov et al. 1993. Chemical Actinometry. In Handbook of Photochemistry. 2nd ed. Marcel Decker Inc., New York. pp. 298-305.
55. Millet et al. 1998. Abiotic Degradation of Halobenzonitriles: Investigations of the Photolysis in Solution. *Ecotoxicol. Environ. Safety.* 41: pp. 44-50.
56. Heller, H. and Langan J. 1981. A new reusable chemical actinometer. EPA Newsletter 71.
57. Bahnemann, D. 1993. Ultra-small metal oxide particles: preparation, photophysical characterization and photocatalytic properties. *Isr. J. Chem.* 33: pp. 115.
58. IUPAC. 1989. Chemical Actinometry. Prepared for publication by H.J. Kuhn, S.E. Braslavsky, and R. Schmidt. *Pure & Appl. Chem.*, Vol. 61, No. 2, (1989) pp. 187- 210.
59. Winterle J and Mill T. 1985. Toxic substances process data generation and protocol development. Work assignment 18: Indirect Photoreaction Protocol. Submitted to Office of Toxic Substances, U.S. Environmental Protection Agency. EPA Contract No. 68-03-2981.

60. IUPAC. 1984. Recommended Standards for Reporting Photochemical Data (1984). *Pure & Appl. Chem.* 56: pp 939- 934.
61. AWWA. 1991. Standard Methods for the Analysis of Water and Wastewater. American Water Works Association, 6666 West Quincy Avenue, Denver, Colorado 80295, USA.
<http://www.awwa.org/stanmeth/contents.htm>
62. Mill T, Mabey W, Winterle J, Davenport J, Barich V, Dulin D, Tse D, and Lee G. 1982. Design and validation of screening and detailed methods for environmental processes. Final Report. Submitted to Office of Toxic Substances, U.S. Environmental Protection Agency. EPA Contract No. 68-01-6325.

ANNEX 1

Definitions and Units

The definitions and units are taken from the Glossary of terms used in photochemistry (IUPAC Recommendations 1996) published in *Pure and Applied Chemistry*, **68**, 2223-2286, 1996. Commonly used and SI units are provided. Cited with permission from the International Union of Pure and Applied Chemistry

Absorbance (A), [Dimensionless] - The logarithm to the base 10 of the ratio of the *spectral radiant power* of incident, essentially monochromatic radiation ($I = \int I_{\lambda} d\lambda$) to the radiant power of transmitted radiation (P):

$$A = \log(P_0/P) = -\log T$$

In practice, absorbance is the logarithm to the base 10 of the ratio of the special radiant power of light transmitted through the reference sample to that of the light transmitted through the solution, both observed in identical cells. T is the (internal) transmittance.

The terms “absorbancy”, “extinction” and “optical density” should no longer be used.

Absorption Coefficient (a), [m^{-1} or cm^{-1}] - *Absorbance* divided by the optical pathlength, l . The term “absorptivity” is not recommended

Actinometer - A chemical system or physical device which determines the number of *photons* in a beam integrally or per unit time and it is commonly applied to devices used in the ultraviolet and visible *wavelength* ranges. Examples of a chemical actinometers are iron(III) oxalate solutions. Examples of physical devices are bolometers, thermopiles and photodiodes. Actinometers give a reading that can be correlated to the number of photons detected.

Beer-Lambert Law - The *absorbance* of a beam of collimated monochromatic radiation in a homogeneous isotropic medium is proportional to the absorption pathlength, l , and to the concentration, c . This law holds only under the limitations of the *Lambert Law* and for absorbing species exhibiting no concentration dependent aggregation. The law can be expressed as,

$$A = \log(P_0/P) = \epsilon \cdot c \cdot l$$

or

$$P = P_0 \cdot 10^{-\epsilon c l}$$

where the proportionality constant, ϵ , is called the *molar (decadic) absorption coefficient*.

Units: For l in cm and c in $mol\ dm^{-3}$ or M , ϵ will result in $dm^3\ mol^{-1}\ cm^{-1}$ or $M^{-1}\ cm^{-1}$. These are the commonly used units. The SI units for ϵ is $m^2\ mol^{-1}$.

Chromophore- That part of a molecular entity consisting of an atom or group of atoms in which the electronic transition responsible for a given spectral band is approximately localized.

Depth of Penetration (of light), [m] - The inverse of the *absorption coefficient*. If the decadic absorption coefficient, a , is used, the depth of penetration ($1/a$) is the distance at which the *spectral radiant power*, P_{λ} , decreases to one tenth of its incident value, P_{λ}^0 .

Einstein - One mole of *photons*. It is not an IUPAC-sanctioned unit. It is sometimes defined as the energy of one mole of photons.

Energy Transfer - From a phenomenological point of view, the term is used to describe the process by which a molecular entity absorbs light and a phenomenon originates from the *excited state* of another molecule. In mechanistic photochemistry, the term has been reserved for the *photophysical process* in which an excited state of a molecular entity (the donor) is deactivated to a lower-lying state by transferring energy to a second molecular entity (the acceptor), which is thereby raised to a higher energy state. The excitation may be electronic, vibrational, rotational or translational. The donor and acceptor may be two parts of the same molecule, in which case the process is called *intramolecular energy transfer*.

Excited State - A state of higher energy than the *ground state* of a chemical entity. In photochemistry an *electronically excited state* is usually meant.

Frequency (ν or ω), [sec^{-1} or $\text{rad}\cdot\text{sec}^{-1}$] - The number of waveperiods per unit time. The linear frequency, ν , is the number of cycles per unit time. For the angular frequency, the symbol ω ($= 2\pi\nu$) is used.

Ground State - The lowest energy state of a chemical entity. In photochemistry, ground electronic state is usually meant.

Half-width (of a band) - The full width of a spectral band at a height equal to half of the height at the band maximum. Also known as *full width at half maximum (FWHM)*. The dimensions of band width should be either inverse length (*wavenumbers*, cm^{-1}) or inverse time (*frequencies*, sec^{-1}) so that the values give an indication of the energies. Note the hyphen in half-width. Half bandwidth has the meaning of half-width at half maximum.

Hyperchromic Effect - Increase in the *intensity* of a band due to substituents or interactions with the molecular environment. Hypochromic effect is the opposite to hyperchromic effect.

Intensity - Traditional term for *photon flux*, *irradiance* or *radiant power (radiant flux)*. In terms of an object exposed to radiation, the term should now be used only for qualitative descriptions.

Intensity (I) (of a light source) - Same as radiant intensity.

Intensity (of a spectral feature) - Describes the magnitude of the particular feature in the spectrum.

Irradiance (E), [W m^{-2}] - The *radiant flux* or *radiant power*, P , of all wavelengths incident on an infinitesimal element of surface containing the point under consideration divided by the area of the element (dP/dS , simplified expression: $E = P/S$ when the radiant power is constant over the surface area considered). $E = \int E_\lambda d\lambda$, where E_λ is the spectral irradiance at wavelength λ . For a parallel and perpendicular incident beam not scattered or reflected by the target or its surrounding *fluence rate* (E_0) is an equivalent term.

Lambert Law - The fraction of light absorbed by a system is independent of the *spectral radiant power* (P_λ^0). This law holds only if P_λ^0 is small, scattering is negligible, and *multiphoton* processes, *excited state* populations, and *photochemical reactions* are negligible.

Lamp - A source of incoherent radiation.

Molar Absorption Coefficient, Molar Decadic Absorption Coefficient - [$\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$, $\text{M}^{-1}\text{cm}^{-1}$ or $\text{dm}^3\text{mol}^{-1}\text{mol}^{-1}$]

Absorbance divided by the absorption pathlength, l , and the concentration,

$$\epsilon = [1 / c l] \log(P_0^0 / P) = A / c l$$

The term molar *absorptivity* for molar absorption coefficient should be avoided.

Photochemical Reaction - This term is generally used to describe a chemical reaction caused by *absorption* of ultraviolet, visible, or infrared radiation.

Photochemistry - The branch of chemistry concerned with the chemical effects of light (far UV to IR).

Photodegradation - The photochemical transformation of a molecule into lower molecular weight fragments, usually in an oxidation process. This term is widely used in the destruction (oxidation) of pollutants by UV-based processes.

Photolysis - A light-induced bond cleavage.

Photon - The *quantum* of electromagnetic energy at a given *frequency*. This energy, $E = h\nu$ is the product of the Planck (h) constant and the *frequency* of the radiation (ν).

Photooxidation - Reactions induced by light. Common process are:

- The loss of one or more electrons from a chemical species as a result of *photexcitation* of that species;
- The reaction of a substance with oxygen under the influence of light. When oxygen remains in the product this latter process is also called *photooxygenation*. Reactions in which neither the substrate nor the oxygen are electronically excited are sometimes called “photoinitiated oxidations”.

Photoreductions - Reduction reactions induced by light. Common process are:

- Addition of one or more electrons to a *photoexcited* species;
- The photochemical hydrogenation of a substance. Reactions in which the substrate is not electronically excited are sometimes called “photoinitiated reductions”.

Photosensitization - The process by which a *photochemical* or *photophysical* alteration occurs in one molecular entity as a result of initial *absorption* of radiation by another molecular entity called a *photosensitizer*. In mechanistic photochemistry the term is limited to cases in which the photosensitizer is not consumed in the reaction.

Primary Photochemical Process (Primary Photoreaction)- Any elementary chemical process undergone by an electronically excited molecular entity yielding a *primary photoproduct*.

Primary (Photo)product - The first observable chemical entity which is produced in the *primary photochemical process* and which is chemically different from the reactant.

Quantum (of radiation) - An elementary particle of electromagnetic energy in the sense of the wave-particle duality.

Quantum Yield (ϕ) - The number of defined events which occur per photon absorbed by the system. The integral quantum yield is:

$$\phi = \text{number of events} / \text{number of photons absorbed}$$

For a *photochemical reaction*,

ϕ = amount of reactant consumed or product formed/amount of photons absorbed

The differential quantum yield is $\phi = d[x]/dt / n$, where $d[x]/dt$ is the rate of change of a measurable quantity, and n is the amount of photons (mol or its equivalent einstein) absorbed per unit time. ϕ can be used for photophysical processes or photochemical reactions.

Radiant Energy (Q), [J] - The total energy emitted, transferred or received as radiation of all wavelengths in a defined period of time ($Q = \int Q_\lambda d\lambda$). It is the product of *radiant power*, and time, $t: Q = P t$ when the radiant power is constant over the time considered.

Radiant Exposure (H), [$J m^{-2}$] - The *irradiance*, E , integrated over time of irradiation ($\int E dt$, simplified expression $H = E t$ when the irradiance is constant over the time considered).

Radiant Intensity (I), [$W sr^{-1}$] - *Radiant (energy) flux or radiation power*, P , at all wavelengths per unit solid angle, ω . The radiant power emitted in a given direction by a source or an element of the source in an infinitesimal cone containing the given direction divided by the solid angle of the cone ($dP/d\omega$, simplified expression: $I = P/S$ when the radiant power is constant over the surface area considered).

Radiant Power (P), [$J s^{-1}$, or W] - Power emitted, transferred or received as radiation.

Singlet Molecular Oxygen - The oxygen molecule (dioxygen), O_2 , in an excited *singlet* state. The *ground state* of oxygen is a triplet ($^3\Sigma_g^-$). The two metastable singlet states derived from the ground state configuration are $^1\Delta_g$ and $^1\Sigma_g^-$.

The IUPAC discourages the use of the term “singlet oxygen” alone, without mentioning the oxygen species (in this case, dioxygen) to avoid confusion with 1S and 1D excited states of the oxygen atom.

Singlet State - A state having a total electron spin quantum number equal to 0.

Solvent Shift - A shift in the *frequency* of a spectral band of a chemical species arising from its interaction with its solvent environment. *Bathochromic shift*, also known to as “red shift”, refers to the shift of a spectral band to lower frequencies (longer wavelengths) as result of interaction with the solvent. *Hypsochromic shift*, also known as “blue shift”, refers to the shift of a spectral band to higher frequencies (shorter wavelengths) as a result of interaction with the solvent..

Spectral Irradiance (E_λ), [$W m^{-3}$, or $W m^{-2} nm^{-1}$] - *Irradiance*, E , at wavelength λ per unit wavelength.

Triplet State - A state having a total spin quantum number of 1.

Wavelength (λ)- The distance, measured along the line of propagation, between two corresponding points on adjacent waves. The wavelength depends on the medium in which the wave propagates

Wavenumber (σ , ν), [m^{-1} or cm^{-1}]- The reciprocal of the wavelength, λ , or the number of waves per unit length along the direction of propagation.

Xenon Lamp - An intense source of ultraviolet, visible and near-infrared light produced by electrical discharge in xenon under high pressure.

ANNEX 2

Symbols and Units Related to Photochemistry

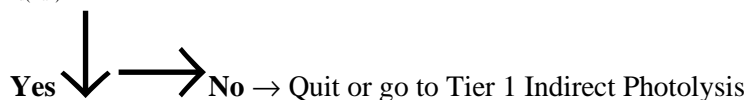
Symbol	Name	SI Units	Common Units
A	Absorbance	Dimensionless	Dimensionless
a	Decadic absorption coefficient	m^{-1}	cm^{-1}
D	Attenuance	Dimensionless	Dimensionless
H_0	Fluence	J m^{-2}	Same
E_0	Fluence rate	W m^{-2}	
E	Irradiance	W m^{-2}	
ϵ	Molar (decadic) absorption coefficient	$\text{m}^{-2} \text{mol}^{-1}$	$\text{cm}^{-1} \text{dm}^3 \text{mol}^{-1}$ <u>or</u> $\text{cm}^2 \text{mmol}^{-1}$ Sometimes $\text{L mol}^{-1} \text{cm}^{-1}$
ϕ	Quantum yield	Dimensionless ^a	Dimensionless ^a
Q	Radiant energy	J	
H	Radiant exposure	J m^{-2}	
I	Radiant intensity	W sr^{-1}	
P	W		
I	Spectral radiance intensity	$\text{W sr}^{-1} \text{m}^{-1}$	$\text{W sr}^{-1} \text{nm}^{-1}$
λ	Wavelength	m	nm
$\sigma; \nu$	Wavenumber	m^{-1}	cm^{-1}

ANNEX 3

Figure 1: Proposed test scheme for direct photolysis

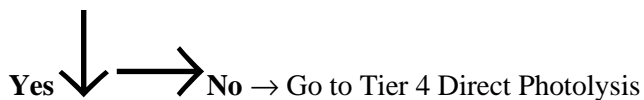
Tier 1 - Theoretical Screen

1. If the test chemical absorbs solar irradiation > 295 nm, estimate a maximum direct photolysis rate constant $K_{d(max)}$ in shallow natural water by assuming the quantum yield $\phi = 1$; $K_{d(max)} = \sum \epsilon_{\lambda} L_{\lambda}$
2. Determine if the maximum direct photolysis rate constant would result in estimated direct photolysis losses of $\geq 20\%$ of an initial concentration over a 30-day/night sunlight exposure period using the following equation: $C/C_0 = \exp [-K_{d(max)} (30\text{-days})]$



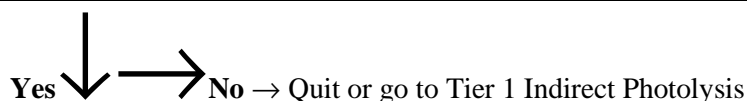
Tier 2 - Experimental Screen

1. Measure the decline of the test chemical in sterilised buffer exposed to a xenon lamp or sunlight. If data fit a first order kinetics model, determine the approximate direct photolysis rate.
2. Determine if approximate direct photolysis rate constant would result in estimated direct photolysis losses of $\geq 10\%$ of an initial concentration from the following equation: $C/C_0 = \exp [-K_{d(max)} (30\text{ days})]$ If yes, go to next step; if no, quit or go to Tier 1 Indirect Photolysis.
3. Is there interest in determining the quantum yield and in estimating theoretical direct photolysis rate constant from the quantum yield?



Tier 3 - Quantum Yield and Estimation of Theoretical Rate constant

1. Determine the quantum yield and use it to estimate theoretical direct photolysis rate constant for seasons, latitudes, elevations and types of water bodies of interest.
2. Is there interest in comparing experimental direct photolysis rate constants with theoretical ones and/or identifying/quantifying major transformation products?



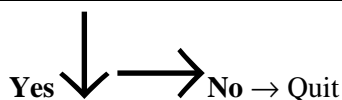
Tier 4 - Determine the Direct Photolysis Rate Constant

1. Measure the decline of the test chemical (and if of interest) the formation and decline of major transformation products in sterilised buffers exposed to a xenon lamp or sunlight.
2. If data fit a first order kinetics model, determine the direct photolysis rate constants and corresponding half-life. Otherwise, determine the DT_{50} , DT_{75} and DT_{90} values from fitting data to a non-first order model. If practical and of interest, determine the same parameters for major transformation products.
3. Is there interest in indirect photolysis? If yes, go to Tier 1 Indirect Photolysis; if no, quit.

Figure 2: Proposed Test Scheme for Indirect Photolysis

Tier 1 - Screen

1. Measure the decline of the test chemical in synthetic water containing humics (and if applicable, nitrate) in buffered distilled water and estimate indirect photolysis rate constant $K_{i(\text{approx})}$.
2. Determine if the approximate indirect photolysis rate constant would result in estimated indirect photolysis losses of $\geq 10\%$ of an initial concentration over a 30-day/night sunlight exposure period using the following equation: $C/C_0 = \exp [-K_{i(\text{approx})} (30 \text{ days})]$
3. In some cases, it may be possible to supplement or even replace the experimental screen with a theoretical screen based on using structural activity relationships (SARs) to estimate second order rate constants and on information on the typical concentrations of photooxidation in surface water.



Tier 2 - Definitive Indirect Photolysis Test

1. Measure the decline of the test chemical (and if of interest) the formation and decline of major transformation products in synthetic and/or natural waters and in buffered distilled water exposure to a xenon lamp or sunlight.
2. If data fit a first order kinetics model, estimate net, indirect, and direct photolysis rate constants and corresponding half-lives for the test chemical. Correct for photobleaching and attenuation effects.
3. If data fit a non-first order model, determine the DT_{50} , DT_{75} and DT_{90} values for fitting data to a non-first order model. If practical and of interest, determine the same parameters for major transformation products.

ANNEX 4

Derivations of Selected Equations

Background equations from Leifer (12):

$$\left(\frac{d[C]}{dt}\right)_\lambda = -\frac{\phi}{j} I_{\lambda(\text{abs by chem})} = -\frac{\phi}{jD_{\text{sys}}} I_{0\lambda} F_{\lambda(\text{abs by sys})} F_{\lambda(\text{abs by chem})}$$

[eq. 3-1]

$$\frac{d[C]}{dt} = -\frac{\phi}{j} \sum_{295}^{800} I_{\lambda(\text{abs by chem})} = -\frac{\phi}{jD_{\text{sys}}} \sum_{295}^{800} I_{0\lambda} F_{\lambda(\text{abs by sys})} F_{\lambda(\text{abs by chem})}$$

[eq. 3-2]

where:

ϕ = quantum yield

j = conversion factor to make units consistent with the L/mol•cm unit of the molar absorption coefficient and the mol/L unit of concentration =
 6.02×10^{20} (L/cm³)(photons/mol)

$I_{\lambda(\text{abs by chem})}$ = photon absorption rate by the chemical per unit volume over a 1 nm interval centered at wavelength λ (photons/cm³•day)

D_{sys} = depth of irradiated system (cm) = volume of irradiated system/incident area

$I_{0\lambda}$ = incident photon flux over a 1 nm interval centered at wavelength λ
 (photons/cm²•day)

$F_{\lambda(\text{abs by sys})}$ = fraction of incident photon flux absorbed by the system

$F_{\lambda(\text{abs by chem})}$ = fraction of incident photon flux absorbed by the chemical

$$F_{\lambda(\text{abs by sys})} = \frac{I_{0\lambda} - I_{t\lambda}}{I_{0\lambda}} = \frac{I_{0\lambda} [1 - 10^{-(\alpha_\lambda + \epsilon_\lambda [C]l)}]}{I_{0\lambda}} = 1 - 10^{-(\alpha_\lambda + \epsilon_\lambda [C]l)}$$

[eq. 3-3]

$$F_{\lambda(\text{abs by chem})} = \frac{\epsilon_\lambda [C]}{\alpha_\lambda + \epsilon_\lambda [C]}$$

[eq. 3-4]

where:

- α_λ = attenuation coefficient of the system at wavelength λ (1/cm)
 ϵ_λ = molar absorption coefficient of the chemical at wavelength λ (L/mol•cm)
 l = light pathlength (cm)

Inserting equations 3-3 and 3-4 into equation 3-1 gives:

$$\left(\frac{d[C]}{dt} \right)_\lambda = - \frac{\phi}{jD_{sys}} I_{0\lambda} [1 - 10^{-(\alpha_\lambda + \epsilon_\lambda [C] l)}] \cdot \left(\frac{\epsilon_\lambda [C]}{\alpha_\lambda + \epsilon_\lambda [C]} \right) \quad [\text{eq. 3-5}]$$

Summing equation 3-5 over all wavelengths from 295 nm to 800 nm gives:

$$\frac{d[C]}{dt} = - \frac{\phi}{jD_{sys}} \sum_{\lambda=295}^{\lambda=800} I_{0\lambda} [1 - 10^{-(\alpha_\lambda + \epsilon_\lambda [C] l)}] \cdot \left(\frac{\epsilon_\lambda [C]}{\alpha_\lambda + \epsilon_\lambda [C]} \right) \quad [\text{eq. 3-6}]$$

For solar irradiation on an aqueous system (12),

$$I_{0\lambda(solar)}(t) = I_{d\lambda}(t) + I_{s\lambda}(t) \quad [\text{eq. 3-7}]$$

$$\bar{l}_d \cong D_{sys} \sec \theta(t) \quad [\text{eq. 3-8}]$$

$$\bar{l}_s = 1.2 D_{sys} \quad [\text{eq. 3-9}]$$

where:

- $I_{0\lambda(solar)}$ = total incident solar photon flux as a function of time
 $I_{d\lambda(solar)}$ = direct incident solar photon flux as a function of time
 $I_{s\lambda(solar)}$ = sky radiation incident solar photon flux as a function of time
 l_d = average light pathlength for direct irradiation
 l_s = average light pathlength for sky irradiation

$$\frac{dC}{dt} = - \frac{\phi}{jD_{sys}} \sum_{\lambda=295}^{\lambda=800} \left\{ I_{d\lambda} [1 - 10^{-(\alpha_\lambda + \epsilon_\lambda [C] D_{sys} \sec \theta)}] + I_{s\lambda} [1 - 10^{-(\alpha_\lambda + \epsilon_\lambda [C] 1.2 D)}] \right\} \left(\frac{\epsilon_\lambda [C]}{\alpha_\lambda + \epsilon_\lambda [C]} \right) \quad [\text{eq. 3-10}]$$

Derivation of equation 5 in the main text (12):

$$10^{-y} = \exp(-2.3y) \quad [\text{eq. 3-11}]$$

Therefore,

$$1 - 10^{-(\alpha_\lambda + \epsilon_\lambda [C])l} = 1 - \exp\{-2.3(\alpha_\lambda + \epsilon_\lambda [C])l\} = 1 - \exp(-x) \quad [\text{eq. 3-12}]$$

where:

$$x = 2.3(\alpha_\lambda + \epsilon_\lambda [C]l) = 2.3A \quad [\text{eq. 3-13}]$$

A = absorbance of the solution

A series expansion of the exponential in equation 3-12 gives:

$$1 - \exp(-x) = x + \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} - \frac{x^5}{5!} + \dots \quad [\text{eq. 3-14}]$$

For an optically dilute solution of a test chemical in pure water or in shallow water or in the near surface of natural water such that the absorbance of the system is < 0.02 , all of the higher terms in equation 3-14 are small compared to x such that equation 3-14 reduces to:

$$1 - \exp(-x) \cong x \quad [\text{eq. 3-15}]$$

Combining equations 3-13 and 3-15 with equation 3-12 gives for an optically dilute solution of a test chemical in pure water or clear shallow water or in the near surface of natural water:

$$1 - 10^{-(\alpha_\lambda + \epsilon_\lambda [C])l} \cong 2.3(\alpha_\lambda + \epsilon_\lambda [C])l \quad [\text{eq. 3-16}]$$

Substituting equation 3-16 into equation 3-6 and canceling out the resulting identical terms in the numerator and denominator gives for an optically dilute solution of a test chemical in pure water or in clear shallow water or in the near surface of natural water:

$$\frac{d[C]}{dt} = -\left(\frac{2.3\phi}{j} \frac{l}{D_{\text{sys}}} \sum_{\lambda=295}^{\lambda=800} \epsilon_\lambda I_{0,\lambda}\right)[C] \quad [\text{eq. 3-17}]$$

By comparing equation 3-17 to equation 1 in the main text, it can be seen that for a test chemical in an optically dilute solution in pure water or in clear shallow water or in the near surface of natural water, the direct photolysis rate constant is given by:

$$k_d = \frac{2.3}{j} \frac{I}{D_{sys}} \phi \sum_{295}^{800} \epsilon_{\lambda} I_{0\lambda} \quad [\text{eq. 3-18}]$$

where equation 3-18 is identical to equation 5 of the main text

Derivation of equation 6 in the main text (12)

By analogy to equation 3-16, it can be seen that for a solar irradiated, optically dilute solution of a test chemical in pure water or in clear shallow water or in the near surface of natural water such that the absorbance of the system is < 0.02 ,

$$1 - 10^{-(\alpha_{\lambda} + \epsilon_{\lambda}[C])D_{sys} \sec \theta} \cong 2.3(\alpha_{\lambda} + \epsilon_{\lambda}[C])D_{sys} \sec \theta \quad [\text{eq. 3-19}]$$

$$1 - 10^{-(\alpha_{\lambda} + \epsilon_{\lambda}[C])(1.2D_{sys})} \cong 2.3(\alpha_{\lambda} + \epsilon_{\lambda}[C])(1.2D_{sys}) \quad [\text{eq. 3-20}]$$

Substituting equations 3-19 and 3-20 into equation 3-10 and canceling out the resulting identical terms in the numerator and denominator gives:

$$\frac{d[C]}{dt} = - \left(\frac{2.3\phi}{j} \sum \epsilon_{\lambda} Z_{\lambda}(t) \right) [C] \quad [\text{eq. 3-21}]$$

where:

$$Z_{\lambda}(t) = I_{di}(t) \sec \theta + 1.2I_{s\lambda}(t) \quad [\text{eq. 3-22}]$$

Equation 3-21 gives the direct photolysis rate as a function of time because the solar photon flux at any given wavelength varies over time as represented by $Z(t)$ for an optically dilute solution.

$$\overline{Z_{\lambda}} = \frac{\int_0^{24} Z_{\lambda}(t) dt}{24 \text{ hours}} \quad [\text{eq. 3-23}]$$

Mill *et al* (1985) defined 24 hour average solar irradiance values as:

$$L_{\lambda} = \frac{2.3}{j} \overline{Z_{\lambda}} \quad [\text{eq. 3-24}]$$

Substituting equation 3-24 into 3-21 gives the average direct photolysis rate over a 24-hour period:

$$\left(\overline{\frac{d[C]}{dt}}\right) = -\left(\phi \sum \varepsilon_{\lambda} L_{\lambda}\right)[C]$$

[eq. 3-25]

By comparing equation 3-25 to equation 1 in the main text, it can be seen that for an optically dilute solution of a test chemical in pure water or clear shallow water or in the near surface of natural water exposed to sunlight, the 24 hour average direct photolysis rate constant is given by:

$$\overline{k_{d(solar)}} = \phi \sum_{295}^{800} \varepsilon_{\lambda} L_{\lambda}$$

[eq. 3-26]

where equation 3-26 is identical to equation 6 in the main text.

Derivation of equation 8 in the main text:

Rearranging equation 3-2 gives the total photon absorption rate per unit volume by the test chemical:

$$I_{(abs \text{ by chem})} = \sum_{295}^{800} I_{\lambda(abs \text{ by chem})} = -\frac{j}{\phi} \frac{d[C]}{dt}$$

[eq. 3-27]

where:

$I_{\lambda(abs \text{ by chem})}$ = photon absorption rate by the chemical per unit volume over a 1 nm interval centered at wavelength λ (photons/cm³•day)

$I_{(abs \text{ by chem})}$ = total photon absorption rate by the chemical per unit volume (photons/cm³•day)

Multiplying equations 3-18 and 3-25 by (-j / .) gives the total photon absorption rate per unit volume by the test chemical in an optically dilute solution exposed to xenon arc lamp or solar irradiation, respectively:

$$I_{(xenon \text{ abs by chem})} = \left(2.3 \frac{I}{D_{sys}} \sum_{\lambda=295}^{\lambda=800} \varepsilon_{\lambda} I_{0\lambda(xenon)}\right) [C_{xenon}]$$

[eq. 3-28]

$$I_{(solar \text{ abs by chem})} = \left(j \sum \varepsilon_{\lambda} L_{\lambda}\right) [C_{solar}]$$

[eq. 3-29]

The total number of photons absorbed per unit volume by a test chemical in a low optical density solution over x days of xenon arc lamp irradiation or over 30 day/nights of solar irradiation are given respectively by:

$$\text{Total \# photons abs by chem / cm}^3 = (X \text{ days xenon}) \left(2.3 \frac{I}{D_{sys}} \sum \varepsilon_{\lambda} I_{0\lambda(xenon)}\right) [\overline{C_{xenon}}]$$

[eq. 3-30]

$$\text{Total \# photons abs by chem / cm}^3 = (30 \text{ days / nights solar}) \left(j \sum \varepsilon_{\lambda} L_{\lambda}\right) [\overline{C_{solar}}]$$

[eq. 3-31]

The number of days (X) of constant irradiation by a filtered xenon arc lamp that is equivalent to 30 days/nights of solar irradiation of a low absorbance water can be obtained by equating equations 3-30 and 3-31, assuming that the average concentration over 30 days/nights of solar irradiation is equal to the average concentration over X days of constant irradiation by a xenon arc lamp, and solving for X:

$$\text{X days xenon} = \left(\frac{30j D_{\text{sys}}}{2.3 l} \right) \left(\frac{\sum \varepsilon_{\lambda} L_{\lambda}}{\sum \varepsilon_{\lambda} I_{0\lambda(\text{xenon})}} \right) = \left(13j \frac{D_{\text{sys}}}{l} \right) \left(\frac{\sum \varepsilon_{\lambda} L_{\lambda}}{\sum \varepsilon_{\lambda} I_{0\lambda(\text{xenon})}} \right)$$

[eq. 3-32]

where equation 3-32 is identical to equation 8 in the main text.

Derivation of equation 10 in the main text:

Substituting equation 3-16 for an optically dilute solution (applicable to a low optical density actinometer solution) into equation 3-5, rearranging and incorporating subscripts to designate the use of monochromatic irradiation from a xenon arc lamp (obtained with a monochromator) gives:

$$\left(\frac{d[C]}{dt} \right)_{\lambda} = - \frac{2.3 \phi_{\text{act}} l}{j D_{\text{sys}}} \varepsilon_{\lambda(\text{act})} I_{0\lambda(\text{xenon})} [C]$$

[eq. 3-33]

By comparing equation 3-33 to equation 1 in the main text, it can be seen that the monochromatic pseudo first order rate direct photolysis rate constant of a low optical density actinometer exposed to monochromatic irradiation from a xenon arc lamp is given by:

$$k_{d\lambda(\text{act})} = - \frac{2.3 l}{j D_{\text{sys}}} \phi_{\text{act}} \varepsilon_{\lambda(\text{act})} I_{0\lambda(\text{xenon})}$$

[eq. 3-34]

Rearranging equation 34 to solve for $I_{0\lambda(\text{xenon})}$ gives:

$$I_{0\lambda(\text{xenon})} = \frac{j D_{\text{sys}} k_{d\lambda(\text{act})}}{2.3 l \phi_{\text{act}} \varepsilon_{\lambda(\text{act})}}$$

[eq. 3-35]

where equation 3-35 is identical to equation 10 in the text.

Derivation of equation 11 in the main text

For a high optical density actinometer solution,

$$10^{-(\alpha_{\lambda} + \varepsilon_{\lambda}[C])l} \cong 0$$

[eq. 3-36]

and

$$\varepsilon_{\lambda}[C] \gg \alpha_{\lambda}$$

[eq. 3-37]

such that

$$\frac{\varepsilon_{\lambda}[C]}{\alpha_{\lambda} + \varepsilon_{\lambda}[C]} \cong \frac{\varepsilon_{\lambda}[C]}{\varepsilon_{\lambda}[C]} = 1$$

[eq. 3-38]

Substituting equations 3-36 and 3-38 for a high optical density actinometer solution into equation 3-6, summing only over the absorption spectrum of the actinometer above 295 nm, and using subscripts to designate the use of a filtered xenon arc lamp gives:

$$\frac{d[C]}{dt} = -\frac{\phi_{act}}{jD_{sys}} \sum_{\lambda=initial}^{\lambda=final} I_{0\lambda(xenon)} \quad [\text{eq. 3-39}]$$

Equation 3-39 is a zero order equation such that the zero order direct photolysis rate constant of the high optical density actinometer is given by:

$$k_{d(act)(zero\ order)} = \frac{\phi_{act}}{jD_{cell}} \sum_{\lambda=initial}^{\lambda=final} I_{0\lambda(xenon)} \quad [\text{eq. 3-40}]$$

Rearranging equation 3-40 gives:

$$\sum_{\lambda=initial}^{\lambda=final} I_{0\lambda(xenon)} = \frac{jD_{cell}}{\phi_{act}} k_{d(act)(zero\ order)} \quad [\text{eq. 3-41}]$$

where equation 3-41 is identical to equation 11 of the main text

Derivation of equation 14 in the main text:

Dividing equation 3-25 (for the pseudo first order rate constant of a test chemical in an optically dilute solution exposed to sunlight) by equation 3-18 (for the pseudo first order rate constant of a test chemical in an optically dilute solution exposed to a filtered xenon arc lamp) and rearranging gives:

$$k_{d(solar)} = \frac{j}{2.3} \frac{D_{cell}}{l} \frac{k_{d(xenon)} \sum_{295}^{800} \epsilon_{\lambda} L_{\lambda}}{\sum \epsilon_{\lambda} I_{0\lambda(xenon)}} \quad [\text{eq. 3-42}]$$

where equation 3-42 is identical to equation 14 in the main text

Derivation of equation 19 in the main text:

By analogy to equation 3-34 for a low optical density actinometer, the monochromatic pseudo first order direct photolysis rate constant of a test chemical in an optically dilute solution exposed to monochromatic irradiation from a xenon arc lamp is given by:

$$k_{d\lambda(chem)} = -\frac{2.3}{j} \frac{l}{D_{sys}} \phi_{chem} \epsilon_{\lambda(chem)} I_{0\lambda(xenon)} \quad [\text{eq. 3-43}]$$

Dividing equation 3-34 by equation 3-43, and rearranging gives:

$$\phi_{chem} = \phi_{act} \frac{k_{d\lambda(chem)} \epsilon_{\lambda(chem)}}{k_{d\lambda(act)} \epsilon_{\lambda(chem)}} \quad [\text{eq. 3-44}]$$

where equation 3-44 is identical to equation 19 of the main text

Derivation of equation 20 in the main text:

Substituting equations 3-36 and 3-38 (for a high optical density actinometer solution exposed to monochromatic irradiation from a xenon arc lamp) into equation 3-5 gives:

$$\left(\frac{d[C]}{dt}\right)_{\lambda} = -\frac{\phi_{act}}{jD_{cell}} I_{0\lambda(xenon)} \quad [\text{eq. 3-45}]$$

Equation 3-45 is a zero order equation such that the monochromatic zero order direct photolysis rate constant of a high optical density actinometer is given by:

$$k_{\lambda(act)(zero\ order)} = \frac{\phi_{act}}{jD_{cell}} I_{0\lambda(xenon)} \quad [\text{eq. 3-46}]$$

Dividing equation 3-43 (for the monochromatic pseudo first order direct photolysis rate constant of a test chemical in an optically dilute solution exposed to monochromatic irradiation from a xenon arc lamp) by equation 3-46 (for the monochromatic zero order direct photolysis rate constant of a high optical density actinometer exposed to monochromatic irradiation from a xenon arc lamp), and rearranging gives:

$$\phi_{chem} = \frac{\phi_{act}}{2.3\epsilon_{\lambda(chem)}D_{cell}} \frac{k_{d\lambda(chem)}}{k_{d\lambda(act)(zero\ order)}} \quad [\text{eq. 3-47}]$$

where 3-47 is identical to equation 20 in the main text

Derivation of equation 21 in the main text:

By analogy to equation 3-46 for a high optical density actinometer, the monochromatic zero order direct photolysis rate constant of a test chemical at high optical density in a solution exposed to monochromatic irradiation from a xenon arc lamp is given by:

$$k_{\lambda(chem)(zero\ order)} = \frac{\phi_{chem}}{jD_{cell}} I_{0\lambda(xenon)} \quad [\text{eq. 3-48}]$$

Dividing equation 3-48 by equation 3-46 and rearranging gives:

$$\phi_{chem} = \phi_{act} \frac{k_{d\lambda(chem)(zero)}}{k_{d\lambda(act)(zero)}} \quad [\text{eq. 3-49}]$$

where equation 3-49 is identical to equation 21 in the main text

Derivation of equation 22 in the main text:

Dividing equation 3-25 (for the pseudo first order rate constant of a test chemical in an optically dilute solution exposed to sunlight) by equation 3-25 (for the pseudo first order rate constant of a low optical density actinometer solution exposed to sunlight), and rearranging gives:

$$\phi_{chem} = \phi_{act} \frac{k_{d(chem)} \sum_{295}^{800} \epsilon_{\lambda(act)} L_{\lambda}}{k_{d(act)} \sum_{295}^{800} \epsilon_{\lambda(chem)} L_{\lambda}} \quad [\text{eq. 3-50}]$$

where equation 3-50 is identical to equation 22 in the main text

Derivation of equation 23 in the main text:

Dividing equation 3-18 (for the pseudo first order rate constant of a test chemical in an optically dilute solution exposed to a filtered xenon arc lamp) by equation 3-18 (for the pseudo first order rate constant of a low optical density actinometer solution exposed to a filtered xenon arc lamp), and rearranging gives:

$$\phi_{chem} = \phi_{act} \frac{k_{d(chem)} \sum_{295}^{800} \epsilon_{\lambda(chem)} I_{0\lambda(xenon)}}{k_{d(act)} \sum_{295}^{800} \epsilon_{\lambda(chem)} I_{0\lambda(xenon)}} \quad [\text{eq. 3-51}]$$

where equation 3-51 is identical to equation 23 in the main text

Derivation of equation 27 In the main text:

Dividing equation 3-25 (for the pseudo first order rate constant for a test chemical in an optically dilute solution in shallow or near to the surface water exposed to sunlight conditions 2) by equation 3-25 (for sunlight conditions 1), and rearranging gives:

$$k_{d(shallow)(solar)2} = k_{d(shallow)(solar)1} \frac{\sum_{295}^{800} \epsilon_{\lambda(chem)} L_{\lambda 2}}{\sum_{295}^{800} \epsilon_{\lambda(chem)} L_{\lambda 1}} \quad [\text{eq. 3-52}]$$

where equation 3-52 is identical to equation 27 in the main text

ANNEX 5

Preparation of Direct Photolysis Test Media

Water meeting ASTM Type IIA standards is recommended to prepare buffer solutions for direct photolysis studies. This water is described in ASTM D 1193-99- Standard Specification for Reagent Water. This document can be obtained from ASTM. In the USA, this document can be obtained from:

American Society for Testing and Materials (ASTM)
1961 Race Street
Philadelphia, Pennsylvania 19103

For outside the USA, see <http://www.astm.org/dist.htm>

A recommended procedure for preparing buffers for direct photolysis studies is given in USEPA OPPTS 835.2210 Direct Photolysis Rate in Water by Sunlight (2). This guideline recommends:

Preparing all buffer solutions at 25° C
Using reagent grade chemicals free of impurities that could behave as photosensitizers
For pHs in the range of 3 to 6, use NaH₂PO₄/HCl
For pHs in the range of 6 to 8, use KH₂PO₄/NaOH
Using procedures such as those described in the Handbook of Chemistry and Physics or by any well establish method.
Always checking the pH with a well calibrated pH meter
Using the minimum concentration of buffer

To prepare the test solutions for the direct photolysis studies, add the buffer solution to the test chemical to attain the desired pH. If necessary, adjust the pH with 1 M HCl or NaOH. It is highly recommended that the actual concentration of the test chemical in the test solution be determined prior to starting the study.

Preparation of Indirect Photolysis Study Test Media

1. SNW (Simulated Natural Water):

- (a) Prepare an initial stock solution of humic acid, followed by filtration, preaging and dilution. The stock solution should have about 60 ppm DOC of humic acid and absorbance of approximately 1.7 at 313 nm and 0.7 at 370 nm. Aging can be accomplished by exposing the stock humic acid solution in a 2-L flask for 3-4 days to direct sunlight (2). The absorbance of the solution is checked and used in estimating a dilution factor for preparing the test solution.
- (b) Buffer the SHW at pH 7 with 0.010 M phosphate solution.
- (c) The SNW test media should have an absorbance of 0.05 at 370 nm and a dissolved organic carbon concentration of about 5 mg/L or ppm.
- (d) The appropriate amount of the test chemical is introduced to the test media immediately prior to irradiation.

2. SNW-N (Simulated Natural Water with Added Nitrate):

- (a) Prepare test media as for SNW, Steps a through c;
- (b) Add nitrate as NaNO_3 or KNO_3 . In freshwater streams of the United States, average nitrate concentrations range from less than 0.1 mg/L to approximately 4 mg/L with the highest concentrations in agricultural followed by urban areas (USGS 1993). The mean nitrate concentration in some lakes may range up to 9 ppm (22). Nitrate concentrations in the agricultural and urban areas of Europe often exceed 9 mg/L (German personal communication).
- (c) The test chemical is introduced immediately prior to irradiation.

3. NW (Natural Water):

Natural surface water may be taken from lakes, rivers, ponds, streams, creeks or coastal water bodies where the test chemical is expected to be present. Proper water sample collection and characterization is required. The geographical location (including longitude and latitude), site characteristics and date of collection should be recorded.

Collection and Sampling

- (a) Sample containers such as polyethylene bottles should be soaked in 10% HNO_3 overnight, thoroughly washed, and then rinsed with distilled water at least three times.
- (b) Samples are collected from the surface (top few centimeters) of the selected water body.
- (c) Water samples that are not used shortly after collection should be stored at 4° C.

Characterization

In the laboratory: The dissolved organic carbon (DOC), pH, and nitrate/nitrite need to be determined (61). As an option, additional factors that influence indirect photolysis can be determined including dissolved oxygen, redox potential, alkalinity, turbidity, other major anions (HCO_3^- , Cl^- , SO_4^{2-}), major cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and other metal ions such as iron and manganese (61).

All waters (SNW, SNW-N, and NW) prepared for the indirect photolysis test should be filter-sterilized with a 0.2 μm filter. The absorptivity should be computed at 350 nm (absorptivity = 2.303 x absorbance/pathlength). Computing the absorptivity at 350 nm in SHW, SHW-N, and NSW provides an estimate of CDOM. CDOM exhibits a much stronger correlation with indirect photolysis rates than DOC.