



Section 3
Environmental fate and behaviour

Test Guideline No. 316

Phototransformation of Chemicals in Water – Direct Photolysis

4 July 2023

**OECD Guidelines for the
Testing of Chemicals**



OECD GUIDELINE FOR THE TESTING OF CHEMICALS

Phototransformation of Chemicals in Water – Direct Photolysis

SCOPE

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 either from direct or indirect (by photosensitizing or reaction with oxidizing transients) aqueous photolysis. This Test Guideline is based on current and /or proposed methods (references (1) - (11)) and on relevant literature on environmental aqueous photochemistry. It deals with direct photolysis.
2. The guideline is divided into the main text and supplementary material
 - The main text describes the
 - Principle of the study
 - The tiered approach (Tier 1: Theoretical screen; Tier 2: Experimental study)
 - Applicability of the Test Guideline, quality criteria and test materials
 - Performance of direct photolysis study
 - Reporting of results
 - Supplementary material provides in
 - Annex 1: A glossary of definitions
 - Annex 2: Symbols and units
 - Annex 3: Derivation of some selected equations
 - Annex 4: Preparation of test media
 - Annex 5: A comparison of monochromatic and polychromatic irradiation
 - Annex 6: Examples of experimental setups

- Annex 7: Examples of selected calculations

INTRODUCTION, ENVIRONMENTAL SIGNIFICANCE AND USE

3. Chemical pollutants and/or their transformation products, which are potentially susceptible to direct photolysis, include those 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 the transformation of other chemicals via hydrolysis, photolysis, and biotransformation.

4. Direct photolysis in natural waters involves the transformation of a chemical resulting from the direct absorption of a solar photon (references (12) - (18)). Accordingly, direct photolysis can be an important dissipation pathway for some chemical pollutants that exhibit significant light absorption above the 290 nm cutoff of solar irradiation at the earth's surface.

5. The direct 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 quantum yield for the photochemical reaction, defined as the fraction of amount of reactant consumed or product formed and the amount of photons absorbed;
- (c) the solar photon irradiance to which the chemical is exposed.

6. The solar photon irradiance, to which a chemical is exposed, depends on numerous factors including latitude, season, and the physical and chemical properties of the water body (12) (18) (19) (20).

7. 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

8. This part of the Test Guideline is designed to provide some or all of the following data and/or information depending upon specific needs:

- 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 < 290 nm will be referred to throughout the rest of the document as a filtered xenon arc lamp).
- The transformation pathway and the identities, concentrations, and rates of formation and decline of phototransformation products resulting from direct photolysis.

- As an optional part 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.

9. This guideline is designed as a tiered approach. Each tier is triggered by the results of the previous tier. The tiered approach for direct photolysis tests is shown in Figure 1.

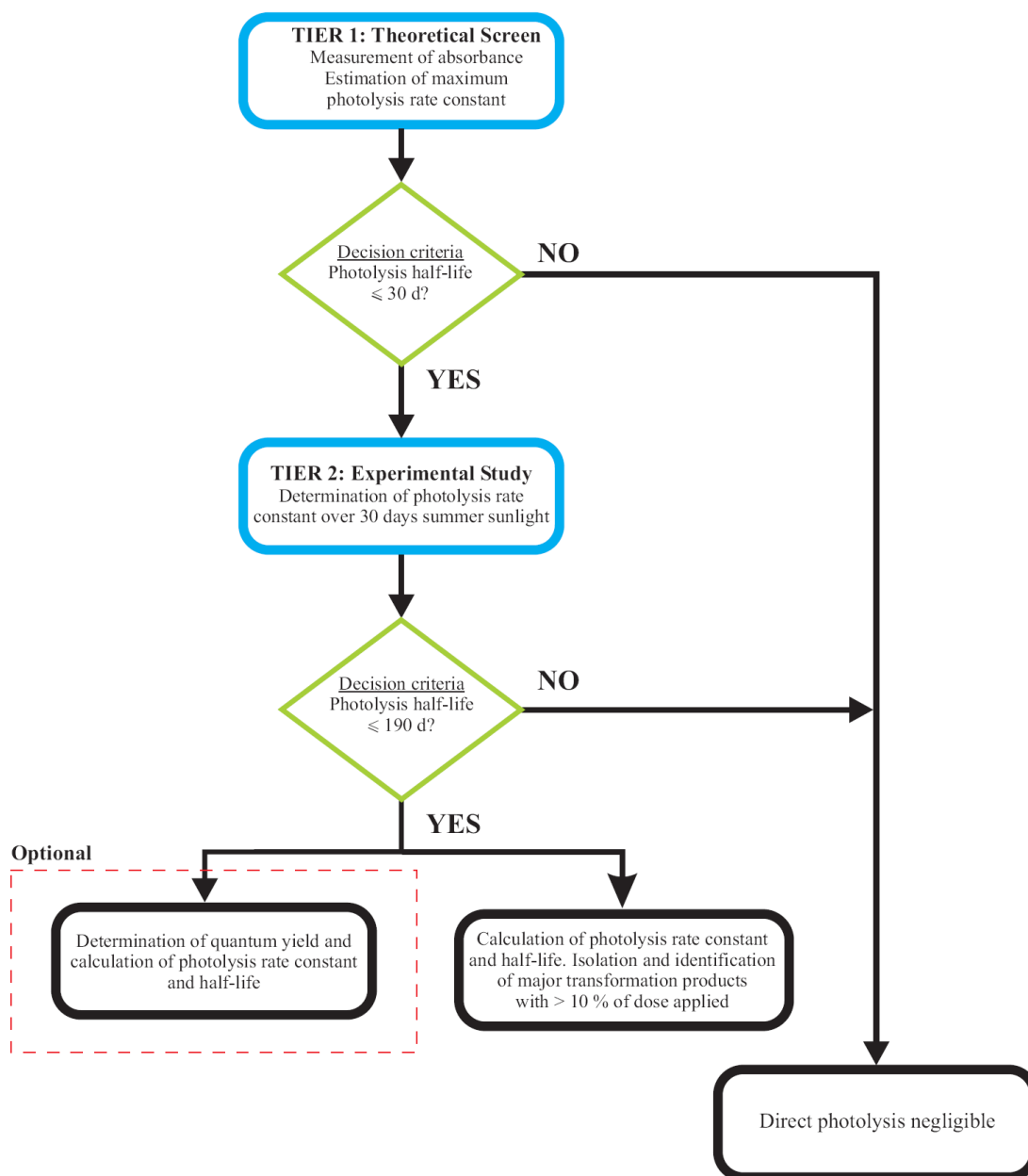


Figure 1: Proposed test scheme for direct photolysis. Test duration of 30 days summer sunlight is defined as 30 days with periods of 12 hours light and 12 hours darkness.

First-order kinetics of direct photolysis

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

$$\frac{dc}{dt} = -k \cdot c \quad 1$$

The integrated form of equation 1 is:

$$c = c_0 \cdot \exp(-k \cdot t) \quad 2$$

The ln transformed version of equation 2 is:

$$\ln(c) = \ln(c_0) - k \cdot t \quad 3$$

The 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 first-order rate constant into the following equation:

$$t_{1/2} = \frac{\ln 2}{k} \quad 4$$

where

c	=	test chemical concentration at time t [mol L ⁻¹]
c ₀	=	initial test chemical concentration at time t = 0 [mol L ⁻¹]
k	=	first-order rate constant [s ⁻¹]
t	=	time [s]
t _{1/2}	=	half-life [s]

Note:

Usually SI-units should be used. However, in the equations provided in this guideline, units for half-lives, first-order rate constants and photon irradiances on number basis are (for illustrative purposes) given in d, d⁻¹, and cm⁻² d⁻¹, respectively. Nonetheless, other units of time such as hours, h, or seconds, s, may be used as long as there is consistency within the same equation. Concentration is used as abbreviation for amount of substance concentration with the unit mol L⁻¹. For clarity the direct photolysis rate constant will be termed *k_d* throughout the rest of the document. For summary of common units used in this guideline but deviating from the SI-system see Annex 2.

Direct photolysis

11. To undergo transformation via direct photolysis, a chemical molecule must first absorb photon(s). The absorption of photon(s) by a molecule results in 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 possible excited electronic state of the molecule (12). Within the UV-Visible wavelength of interest

(290-800 nm), molar photon energies range from 150 kJ mol⁻¹ at 800 nm to slightly greater than 400 kJ mol⁻¹ at 290 nm (11) (21).

12. The absorption of a photon is necessary, but often not sufficient condition, for molecule to undergo transformation via direct photolysis (12) (14) (21). 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 (i.e. the quantum yield) is generally much less than 1 (usually < 0.1 and sometimes < 0.01) (14) (22). The mechanistic aspects of phototransformation reactions at molecular level are beyond the scope of this guideline (see reference (23) for further information).

13. It can be shown that for an optically dilute solution (decadic absorbance $A_\lambda < 0.02$ for $\lambda \geq 290\text{nm}$) of a chemical in pure water exposed to polychromatic irradiation above the cutoff of solar irradiation at the earth's surface of 290 nm, the direct photolysis rate constant (assuming the quantum yield is independent of wavelength) is given by (12) (14) -(18) (see Annex 3, Derivations of Selected Equations):

$$k_d = 2.3 \cdot \frac{l}{D_{sys}} \Phi \sum_{290}^{800} \epsilon_\lambda \cdot I_{0\lambda} \quad 5$$

where:

- k_d = direct photolysis rate constant [d⁻¹]
- Φ = quantum yield (independent of wavelength)
- ϵ_λ = molar decadic absorption coefficient [L mol⁻¹ cm⁻¹] at wavelength λ
- $I_{0\lambda}$ = photon irradiance, on amount basis [mmol cm⁻² d⁻¹] over a 1 nm interval centered at wavelength λ
- l = light pathlength [cm]
- D_{sys} = depth of irradiated system [cm] = volume of irradiated system/incident area

Note: The term (l/D_{sys}) in equation approximately cancels out for rectangular photolysis cells exposed to irradiation from filtered xenon arc lamp and for which $D_{sys} = D_{cell}$. However, that would not be true for cylindrical photolysis cells or for any photolysis cells exposed to solar irradiation where the pathlength has 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 function of the depth of 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. The determination of molar decadic absorption coefficients is described in detail in OECD Guideline 101 (UV-VIS Absorption Spectra).

14. 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 3, Derivations of Selected Equations):

$$k_{d(solar)} = \Phi \sum_{\lambda = 290}^{\lambda = 800} \epsilon_{\lambda} \cdot L_{\lambda} \quad 6$$

where:

$k_{d(solar)}$	=	direct photolysis rate constant [d^{-1}]
Φ	=	quantum yield (independent of wavelength)
ϵ_{λ}	=	molar decadic absorption coefficient [$L \text{ mol}^{-1} \text{ cm}^{-1}$] at wavelength λ
L_{λ}	=	average daily solar photon irradiance, on amount basis [$\text{mmol cm}^{-2} \text{ d}^{-1}$] over wavelength interval $\Delta\lambda$ centered at wavelength λ

15. Equations 1, 5 and 6 show that direct photolysis kinetics are theoretically first order only if the photon irradiance remains constant over time. Photon irradiances 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 irradiances 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, first-order rate constant model reasonably well. The reason is that changes in the average 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

16. 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 decadic absorption coefficients from 290 nm to 800 nm, and use tabular solar irradiance for summer and (preferably) 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 decadic absorption coefficients and tabular solar irradiance values, L_{λ} , into equation 6 (2) (12). Determine the corresponding half-life. If the half-life is > 30 d, no further direct photolysis work is performed. If the half-life is ≤ 30 d, proceed to Tier 2 (experimental study).

Tier 2 -Experimental study

Determination of the direct photolysis rate constant

17. 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. Using these data estimate the half-life of the chemical which results under summer sunlight in the near surface of a clear natural water body. If this half-life is > 190 d, no further work on direct photolysis is

performed. If this half-life is ≤ 190 d, identify major transformation products. An optional task is the additional determination of the quantum yield.

Identification of major transformation products

18. Determine the rate of formation and decline of phototransformation products (if possible) of the test chemical in buffered pure water exposed to a filtered xenon arc lamp (recommended) or sunlight. Isolate and identify the major transformation products. In this guideline, major transformation products are defined as those accounting for 10% (on amount basis) of the applied test chemical in an individual sample at any sampling time.

Determination of the quantum yield and its use to estimate direct photolysis rate constants (optional)

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). The first-order rate constant for direct phototransformation and thus the life-time of a test chemical in water can be calculated from the quantum yield (18) (24). Hence, once the quantum yield has been determined, use it as input to computer programs such as GCSOLAR¹ (18) or ABIWAS² (19) (20) to help to estimate direct photolysis rates and half-life for the test chemical applicable to any types of surface waters (defined by depth and light attenuation), seasons, and latitudes of interest (2).

APPLICABILITY OF THE TEST GUIDELINE

20. 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.

21. 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) (25). 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 test chemical may undergo rapid hydrolysis (i.e., hydrolysis half-life of < 1 d) within the environmentally relevant pH range of 4-9 at 20-25 °C (26). In such cases, the photolysis study should instead be conducted on the major hydrolysis product(s) ($\geq 10\%$ (on amount basis) of applied as the test chemical). For non-ionic test chemicals soluble in water and which are not hydrolyzed in water, photolysis can be performed in pure water to avoid possible influences of the buffer.

22. 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

¹ The latest version of the program GCSOLAR is available from the EPA Center for Exposure Assessment Modeling (CEAM): <http://www.epa.gov/ceampubl/swater/gcsolar/index.htm>

² The latest version of the program ABIWAS is available from the Fraunhofer Institute for Molecularbiology and Applied Ecology, 57377 Schmallenberg, Germany

numerous small photolysis cells than when employing aliquot sampling on smaller number of much larger test vessels. However, with the proper equipment and experimental set-up, it can be done as shown by Ruzo (27).

23. Unlabelled or labelled test chemicals can be used to measure the rate of phototransformation. Labelled material is required for studying the pathway of phototransformation and for establishing a mass balance. ^{14}C -labelling is recommended but other isotopes, such as ^{13}C , ^{15}N , ^{32}P , may also be useful. As far as possible, the label should be positioned in the most stable part(s) of the molecule³. The chemical and radiochemical purity of the test chemical should be at least 95%.

24. Before carrying out any of the phototransformation tests, the following information on the test chemical should be available:

- (a) Solubility in water [OECD Guideline 105].
- (b) Solubility in organic solvents
- (c) Vapor pressure [OECD Guideline 104]
- (d) Henry's Law Constant⁴
 - (e) Abiotic hydrolysis as a function of pH [OECD Guideline 111]
 - (f) n-octanol/water partition coefficient [OECD Guidelines 107 and 117]
 - (g) pKa(s) of ionisable substances [OECD Guideline 112]

Note: The temperatures at which the physical chemical properties listed above were determined should generally be 25 °C, deviations from this temperature should be reported.

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

26. An appropriate analytical method of known accuracy, precision and sensitivity for the quantification and identification of the test chemical and its phototransformation products should be available. The analytical detection limit for the test chemical and its phototransformation products should also be known (see paragraph 30).

REFERENCE SUBSTANCES

27. Reference substances should be used for the characterisation and/or identification of phototransformation products by spectroscopic and chromatographic methods.

³ For example, if the test chemical contains one ring, labelling on this ring is required; if the test chemical contains two or more rings, separate studies may be needed to evaluate the fate of each ring and to obtain suitable information on formation of phototransformation products.

⁴ 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>

QUALITY CRITERIA

Recovery

28. Extraction and analysis of, at least, duplicate samples immediately after the addition of the test chemical gives a first indication of the repeatability of the analytical method and of the initial recoveries for the test chemical. Recoveries for later stages of the experiments are given by the respective mass balance obtained with labelled material. Recoveries should range from 90% to 110% for labelled chemicals and from 70% to 120% for non-labelled chemicals.

Repeatability and sensitivity of analytical method

29. Repeatability of the analytical method (excluding the initial extraction efficiency) to quantify test chemical and phototransformation products can be checked by duplicate analysis of the same extract, incubated long enough for formation of phototransformation products.

30. The limit of detection (LOD) of the analytical method for the test chemical and for the phototransformation products should be at least 10^{-7} mol L⁻¹ in water (as test chemical) or 1% of the applied dose whichever is lower. The limit of quantification (LOQ) should also be specified.

Accuracy of transformation data

31. Regression analysis of the concentration of the test chemical as a function of time gives the appropriate information on the reliability of the phototransformation curve and allows the calculation of the confidence limits for half-lives (in case of first-order kinetics) or DT50 values and, if appropriate, DT90 values.

TEST MATERIALS

Test vessels

32. Quartz tubes are recommended for the photolysis of chemicals with appreciable absorption at wavelengths below 340 nm. Chemicals that absorb appreciably at wavelengths greater than 340 nm may be tested in borosilicate tubes. (2)

33. All glassware and reaction vessels/photolysis cells used in the photolysis studies should be sterilized by autoclaving (2) (3) (4) (12) or any other suitable non-chemical method (2). Chemical sterilization is not recommended since chemical reagents may leave residues that could absorb in the 290 to 800 nm region and/or behave as photosensitizers.

Test chemical application

34. The test chemical should be directly dissolved in the aqueous media at a concentration which should not exceed half its solubility. 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 (25). The selected co-solvent must not solvolyse the test chemical, must not absorb in the 290 to 800 nm region, and must not be a photosensitizer. A general discussion of photosensitizers with numerous examples can be found in (23).

Acetone is an example of a solvent that is a photosynthesizer, and should not be used. Acetonitrile is a generally recommended co-solvent.

35. The initial concentration of the test chemical for quantum yield determinations and direct photolysis studies should be such that the decadic absorbance at any wavelength above 290 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 $< 10^{-4}$ mol L⁻¹. Nevertheless, the initial concentration of the test chemical should be at least 10 times greater than the quantification limit of the analytical method.

36. 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.

Test media for direct photolysis studies

37. Guidance for preparing test media for direct photolysis is provided in Annex 4.

38. For direct photolysis studies, the test media should be sterilized aqueous buffer solutions at the appropriate pH (for sterilisation methods see paragraph 33). The water should be "pure water". The buffers should be identical or comparable to those used in the hydrolysis studies (26) and should not absorb between 290 and 800 nm or be photosensitizers. Also, the buffers should not adversely affect the solubility of the test chemical.

39. For non-ionisable test chemicals the tests should be conducted at a pH at which the test chemical is hydrolytically most stable in the pH range 4-9.

40. If the test chemical is appreciably ionic anywhere within a 4 to 9 pH range, the study should be conducted in one or more aqueous buffers at any of the pH 4, 7, and/or 9. Selection of the pH at which the study should be conducted depends on the electronic absorption spectra at each pH. If the molar decadic absorption coefficient of the test chemical λ for $\lambda \geq 290$ nm is below the trigger value of 10 L mol⁻¹ cm⁻¹, a study at this particular pH is not necessary. Refer to Tier 1 and paragraph 67 for further details.

Light sources

41. The photon irradiance of a light source is determined by a chemical actinometer (rather rarely by a spectral radiometer). An actinometer is a chemical system for the determination of the number of photons integrally or per time interval absorbed into the defined space of a chemical reactor (see also Annex 1). Suitable actinometers are summarized in Table 2 (Annex 5). Experimental details (use, preparation of solutions) of the most common used actinometer can be found in (28).

42. For direct photolysis studies the recommended light source should be a filtered xenon arc lamp capable of simulating natural sunlight in the 290 to 800 nm region or sunlight (29). The photon irradiance 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 or a spectral radiometer. If sunlight is used, average daily solar photon irradiances (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. In addition for sunlight experiments the cloud cover should be reported.

43. If a filtered xenon arc lamp is used, the photon irradiance 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 irradiance to lamp photon irradiance because of the linear relationship between the transformation rate and photon irradiance (see equation 12).

44. If a filtered xenon arc lamp (see Annex 6) 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 photon irradiance. Self-contained, commercially available xenon photolysis units in the projection or "working plane" configuration produce uniform irradiances (30) (31). A commonly used configuration is the "merry-go-round" photochemical reactor (12). Merry-go-round photochemical reactors are commercially available (31) (32) (see Annex 6). Besides the "merry-go-round" the second often used experimental setup is an "optical bench", discussed in Annex 6. Another example of an experimental set-up is shown in reference (24) and an experimental set-up that includes trapping of volatiles appears in references (27).

Other photolytic equipment and reagents

45. Photolytic equipment includes:

- Optical cells of appropriate material (generally quartz) and path length for measuring UV-VIS spectra.
- Appropriate optical filters to cut-off radiation below 290 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) (29). 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. An example of a useful optical bench is shown in Annex 6. (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 shown in Annex 6.
- Photometer or spectral radiometer to measure photon irradiance as a function of wavelength.

46. 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 4: 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.
- Appropriate aqueous buffers such as phosphate for pH 7, acetate for pH 4 and borate for pH 9 for compatibility with hydrolysis studies. Phosphate buffers are usually recommended for direct

photolysis studies (2) (12) but only cover pH range 5 to 8. Caution should be applied when using phosphate buffers because they might promote catalytic effects.

Analytical equipment and chemical reagents

47. 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 chemical 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 chemicals 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.
48. Chemical reagents include:
- Reagent grade chemicals and solvents free of any photosensitizer
 - Scintillation liquid (for radiolabelled chemicals).

TEST METHODOLOGY

Test conditions

49. The temperature during photolysis studies may vary by as much as 10 degrees but should be maintained within the range of 23 to 27 °C. (25 ± 2)°C and monitored periodically.
50. The variation of the pH of buffered solutions should not exceed 0.2. The pH should be checked during the course of the study, if feasible.
51. Dark control solutions should be used for all quantum yield determinations and for all direct photolysis studies and should be kept at the same temperature as the irradiated samples.

Study duration, sampling, and replication

52. A sunlight day is defined throughout the guideline as a day with periods of 12 hours light and 12 hours dark.
53. 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 < 0.25 of their maximum concentration. However, the maximum study duration

should not exceed the equivalent of 30 days of sunlight exposure during an appropriate season and at an appropriate latitude.

54. Based upon equating photons absorbed by the test chemical, the maximum direct photolysis study duration (using continuous filtered xenon arc lamp irradiation) that is equivalent to 30 days of sunlight exposure will be only a few days and is given by (see Annex 3, Derivations of Selected Equations):

$$\text{max. direct photolysis duration (d)} = \frac{30 D_{\text{cell}} \sum_{290}^{800} \epsilon_{\lambda} L_{\lambda}}{2.3 I_{\text{xenon}} \sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda}} \quad 7$$

where:

- 30 = 30 d of solar irradiation
- D_{cell} = depth of irradiated cell [cm] = volume of irradiated cell/incident area
- I_{xenon} = light pathlength in cell [cm] exposed to a filtered xenon arc lamp
- ϵ_{λ} = molar decadic absorption coefficient [$\text{L mol}^{-1} \text{cm}^{-1}$] at wavelength λ
- $I_{0\lambda}$ = photon irradiance, on amount basis [$\text{mmol cm}^{-2} \text{d}^{-1}$] over a 1 nm interval centered at wavelength λ
- L_{λ} = average daily solar photon irradiance, on amount basis [$\text{mmol cm}^{-2} \text{d}^{-1}$] over wavelength interval $\Delta\lambda$ centered at wavelength λ

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

55. Although equation 7 allows for flexibility in choosing an experimental photon irradiance from a filtered xenon arc lamp, practical considerations somewhat limit the range of experimental irradiances that should be used. In general, it is recommended that the experimental photon irradiance 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 irradiance 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.

56. A preliminary range-finding study may 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.

57. 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.

58. Replicates (preferably a minimum of two) of irradiated and dark controls 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 pros and cons of experimental replication versus increased numbers of sampling times per experiment should be weighted in designing the study.

Calculations

59. Calculations/equations for the kinetics of the formation and decline of major photoproducts 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 irradiance from a filtered xenon arc lamp

60. The photon irradiance for a given wavelength interval 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 (33). The advantage in using a spectral radiometer to determine the photon irradiance for a given wavelength interval 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 irradiance, it should be periodically calibrated against photon irradiances 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 (33).

61. By determining the monochromatic first-order direct photolysis rate constant for a low optical density actinometer of known quantum yield in pure water in a photolysis cell irradiated with monochromatic irradiation, the incident photon irradiance at the wavelength of the irradiation can be determined from the following equation (33):

$$I_{0\lambda(\text{xenon})} = \frac{1}{2.3} \frac{D_{\text{cell}}}{l_{\text{xenon}}} \frac{k_{d\lambda(\text{act})}}{\Phi_{\text{act}} \epsilon_{\lambda(\text{act})}} \quad 8$$

where:

$I_{0\lambda(\text{xenon})}$ = photon irradiance, on amount basis [mmol cm⁻² d⁻¹] over a 1 nm interval centered at wavelength λ

$k_{d\lambda(\text{act})}$ = monochromatic direct photolysis rate constant ([d⁻¹], first order) of an actinometer exposed to monochromatic irradiation at wavelength λ

Φ_{act}	=	the quantum yield of the actinometer
$\epsilon_{\lambda(act)}$	=	molar decadic absorption coefficient [$L \text{ mol}^{-1} \text{ cm}^{-1}$] of the actinometer at wavelength λ
D_{cell}	=	depth of irradiated cell [cm] = volume of irradiated cell/incident area
l_{xenon}	=	light pathlength [cm] in cell exposed to monochromatic irradiation

62. Equation 8 only gives the photon irradiance 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 irradiance at several different individual wavelengths spread throughout the wavelength range in which an estimate of the photon irradiance is desired should be sufficient to determine the photon irradiance from a filtered xenon arc lamp as a continuous function of wavelength. Because photon irradiance from a filtered xenon arc lamp is smooth, interpolation from known photon irradiances at several different wavelengths can be readily done (33).

63. By determining the polychromatic zero-order direct photolysis rate constant for a high optical density actinometer of known quantum yield in pure water in a photolysis cell irradiated with a filtered xenon arc lamp, the sum of the incident photon irradiance over the absorption spectrum of the actinometer above 290 nm can be determined from the following equation (33):

$$\sum_{\lambda = \text{initial}}^{\lambda = \text{final}} I_{0\lambda(xenon)} = \frac{D_{cell}}{\Phi_{act}} k_{d\lambda(act)(zero\ order)} \quad 9$$

where:

$\lambda = \text{initial}$	=	initial wavelength of actinometer absorption (if ≥ 290 nm)
$\lambda = \text{final}$	=	final wavelength of the actinometer absorption (if ≤ 800 nm)
$I_{0\lambda(xenon)}$	=	photon irradiance, on amount basis [$\text{mmol cm}^{-2} \text{ d}^{-1}$] over a 1 nm interval centered at wavelength λ
D_{cell}	=	depth of irradiated cell [cm] = volume of irradiated cell/incident area
Φ_{act}	=	the quantum yield of the actinometer
$k_{d\lambda(act)(zero\ order)}$	=	monochromatic direct photolysis rate constant (zero order) of an actinometer exposed to monochromatic irradiation at wavelength λ [$\text{mol L}^{-1} \text{ d}^{-1}$]

64. By using more than one high optical density actinometer with absorption bands at different wavelengths, the sum of the photon irradiances over any desired range including the entire range between 290 and 800 nm can be determined. Further experimental details of procedures for determining the photon irradiance from and for calibrating xenon arc lamps are provided in references (19) (33) (34) (35).

Performance of direct photolysis study

Tier 1 -Theoretical screen.

65. For a test chemical which does not ionize significantly within a pH range of 4 to 9, a single UV-Visible absorption spectrum should be measured at a single pH within the 4 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 4 to 9 pH range, UV-Visible absorption spectra should be measured at pH 4, 7, and 9.

66. Electronic absorption spectra of the test chemical should be obtained in appropriate solvent systems at desired pH with a spectrometer capable of recording UV-VISIBLE spectra between 290 and 800 nm. Because the higher energy (shorter wavelength) bands of many chemicals may sometimes tail into wavelengths above 290 nm, it is recommended that the spectrum be recorded 30 to 40 nm below 290 nm. The procedure to record, assign absorption band maxima, band-widths and determine molar decadic 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 chemical be also obtained in the pure co-solvent.

67. If the test chemical absorbs above the 290 nm cutoff of solar irradiation ($\lambda \geq 290$ nm) at the earth's surface with $\epsilon_{\lambda} > 10 \text{ L mol}^{-1} \text{ cm}^{-1}$, estimate a maximum possible direct photolysis rate by assuming that the quantum yield is equal to one in equation 6 (2):

$$k_{d(\max)} = 2.303 \sum_{\lambda=290}^{\lambda=800} \epsilon_{\lambda} \cdot L_{\lambda} \quad 10$$

where:

$k_{d(\max)}$ = maximum possible direct photolysis rate constant [d^{-1}]

ϵ_{λ} = molar decadic absorption coefficient [$\text{L mol}^{-1} \text{ cm}^{-1}$] at wavelength λ

L_{λ} = average daily solar photon irradiance, on amount basis [$\text{mmol cm}^{-2} \text{ d}^{-1}$]

over wavelength interval $\Delta\lambda$ centered at wavelength λ .

68. In estimating the maximum possible photolysis rate constant, the average daily solar photon irradiances L_{λ} substituted into equation 10 should be those for summer at (preferably) 40° or 50° latitude. Values of L_{λ} can be readily obtained from tables (2) (12) (18). As an alternative to the use of equation 10 and tables of L_{λ} , the maximum direct photolysis rate constant can be readily estimated by inputting molar decadic absorption coefficients and a quantum yield equal to one into computer programs such as GCSOLAR (18) or ABIWAS (19) (20).

Criteria for deciding whether to go to Tier 2

69. Determine 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 irradiance from equation 10.

70. If the estimated half-life (assuming a maximum direct photolysis rate constant) is > 30 d, direct photolysis is considered to be an insignificant process. In such a case, no further direct photolysis work is performed.

71. If the estimated half-life (assuming a maximum direct photolysis rate constant) is lower than or equal to 30 d, go to Tier 2 (experimental study).

Tier 2 -Experimental study

72. If the test chemical is appreciably ionic anywhere within a 4 to 9 pH range, the study should be conducted in one or more aqueous buffers at any of the pH 4, 7, and/or 9. However, if the molar decadic absorption coefficient of the test chemical λ for $\lambda \geq 290$ nm is below the trigger value of $10 \text{ L mol}^{-1} \text{ cm}^{-1}$, a study at this particular pH is not necessary.

73. 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 of the test vessels to serve as dark controls. To account for volatile losses of test chemical and /or transformation products, test vessels should be attached to suitable traps for the collection of organic volatiles and CO_2 .

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

75. 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.

76. If the data follow first-order kinetics, compute irradiated and dark control rate constants for the test chemical using linear regression on log transformed data as shown in equation 3 or non-linear regression on non-transformed data as shown in equation 2.

77. 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:

$$k_d = k_{\text{irradiated}} - k_{\text{dark}} \quad 11$$

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

78. Estimate a direct photolysis rate constant for the test chemical in near surface clear natural water exposed to average daily solar photon irradiances L_λ from the direct photolysis rate constant in a photolysis cell exposed to continuous photon irradiances from a filtered xenon arc lamp using the following equation (see Annex 3, Derivations of Selected Equations):

$$k_{d(solar)} = \frac{1}{2.3} \cdot \frac{D_{cell}}{l} \frac{k_{d(xenon)} \sum_{290}^{800} \epsilon_{\lambda} L_{\lambda}}{\sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda(xenon)}} \quad 12$$

where:

$k_{d(solar)}$ = average daily direct photolysis rate constant [d^{-1}] for the test chemical in the near surface of clear natural water exposed to average daily solar photon irradiances L_{λ}

$k_{d(xenon)}$ = direct photolysis rate constant [d^{-1}] for the test chemical in buffered pure water in photolysis cells exposed to constant filtered xenon arc lamp irradiances $I_{0\lambda(xenon)}$

ϵ_{λ} = molar decadic absorption coefficient of the test chemical
[$L \text{ mol}^{-1} \text{ cm}^{-1}$] at wavelength λ

D_{cell} = depth of irradiated cell [cm] = volume of irradiated cell/incident area

l = light pathlength in cell exposed to a filtered xenon arc lamp [cm]

$I_{0\lambda(xenon)}$ = incident filtered xenon arc lamp photon irradiance, on amount basis
[$\text{mmol cm}^{-2} \text{ d}^{-1}$] over a 1 nm interval centered at wavelength λ

L_{λ} = 24 hour average daily solar photon irradiance, on amount basis [$\text{mmol cm}^{-2} \text{ d}^{-1}$] over wavelength interval $\Delta\lambda$ centered at wavelength λ for the weakly absorbing near surface of clear natural water bodies

79. To use equation 12, the photon irradiance 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 or a spectral radiometer. The solar photon irradiances 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 identify major transformation products and (optional) to determine quantum yields

80. Calculate the half-life of the chemical by using the direct photolysis rate constant for the test chemical in the near surface of a clear natural water exposed to sunlight.

81. If this half-life is > 190 d, direct photolysis is considered to be an insignificant process. In such a case, no further direct photolysis work is performed.

82. If this half-life is ≤ 190 d, identify major transformation products and (optional) determine the quantum yield.

Identification of major transformation products

83. In Tier 2 the test chemical in buffered pure water is exposed to a filtered xenon arc lamp or sunlight. The rates of formation and decline of transformation products are determined, if possible. Major phototransformation products are isolated and identified. For the purposes of this guideline, a major transformation product is one accounting for 10% of the applied radioactivity (on amount basis) as a mean of replicates at any time during the study.

84. If a flow-through system is used to trap volatile test chemicals and/or their 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.

85. 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.

86. Determine the concentrations of the transformation products in the irradiated test vessels and in the dark control test vessels at adequate sampling intervals.

87. 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.

88. Identify and quantify major phototransformation products using analytical methods and criteria indicated in paragraph 26.

89. 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 10% on amount basis of applied) after the parent has degraded to negligible levels.

90. 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.

Determination of the quantum yield (optional)

91. 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 (see Annex 5).

Determination of the quantum yield using monochromatic irradiation

92. Place solutions of the test chemical and the selected optically low density actinometer in separate but identical photolysis cells. A compilation of common actinometers can be found in Annex 5. 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 chemical in the irradiated cells and in the dark controls at adequate sampling

intervals to determine the monochromatic direct photolysis rate constant of the test chemical ($k_{d\lambda(\text{chem})}$) 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.

93. The decline of a test chemical or actinometer concentrations at low optical density should follow 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:

$$c = c_0 - k \cdot t \quad 13$$

94. 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 ($k_{d\lambda(\text{chem})}$) and of the actinometer ($k_{d\lambda(\text{act})}$) at wavelength λ are given by:

$$k_{d\lambda(\text{chem or act})} = k_{\lambda(\text{irradiated})(\text{chem or act})} - k_{\lambda(\text{dark})(\text{chem or act})} \quad 14$$

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.

95. Determine the molar decadic absorption coefficients of the test chemical ($\epsilon_{\lambda(\text{chem})}$) and (if a low optical density actinometer is being used) of 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:

$$\epsilon_{\lambda(\text{chem or act})} = \frac{A_{\lambda(\text{chem or act})}}{l \cdot c_{(\text{chem or act})}} \quad 15$$

where:

$\epsilon_{(\text{chem or act})}$	=	molar decadic absorption coefficient of the test chemical or actinometer [L mol ⁻¹ cm ⁻¹] at wavelength λ
$A_{\lambda(\text{chem or act})}$	=	decadic absorbance of test chemical or actinometer solution at wavelength λ
l	=	light pathlength [cm] generally equivalent to D_{cell}
D_{cell}	=	depth of irradiated cell [cm] = volume of irradiated cell/incident area
$c_{(\text{chem or act})}$	=	concentration of test chemical or actinometer solution [mol L ⁻¹]

96. The quantum yield of an optically dilute test chemical determined using monochromatic irradiation and a low optical density (low decadic absorbance) actinometer is given by (12) (29):

$$\Phi_{chem} = \Phi_{act} \frac{k_{d\lambda(chem)} \epsilon_{\lambda(act)}}{k_{d\lambda(act)} \epsilon_{\lambda(chem)}} \quad 16$$

where:

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

97. The quantum yield of an optically dilute test chemical determined using monochromatic irradiation and a high optical density (high decadic absorbance) actinometer is given by (12) (29):

$$\Phi_{chem} = \frac{\Phi_{act}}{2.3 \epsilon_{\lambda(chem)} D_{cell}} \frac{k_{d\lambda(chem)}}{k_{d\lambda(act)(zero\ order)}} \quad 17$$

where:

Φ_{chem}	=	the quantum yield of the test chemical
Φ_{act}	=	the quantum yield of the actinometer
$\epsilon_{\lambda(chem)}$	=	molar decadic absorption coefficient of the test chemical [$L \text{ mol}^{-1} \text{ cm}^{-1}$] at wavelength λ
$k_{d\lambda(chem)}$	=	monochromatic direct photolysis rate constant ($[d^{-1}]$, first-order) of a test chemical exposed to monochromatic irradiation at wavelength λ
$k_{d\lambda(act)(zero\ order)}$	=	monochromatic direct photolysis rate constant ($[mol \text{ L}^{-1} \text{ d}^{-1}]$, 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

98. The quantum yield of a test chemical at high optical density (high decadic absorbance) determined using monochromatic irradiation and a high optical density (high decadic absorbance) actinometer is given by (12) (29):

$$\Phi_{chem} = \Phi_{act} \frac{k_{d\lambda(chem)(zero\ order)}}{k_{d\lambda(act)(zero\ order)}} \quad 18$$

where:

Φ_{chem} = the quantum yield of the test chemical
 Φ_{act} = the quantum yield of the actinometer
 $k_{d\lambda(chem)(zero\ order)}$ = monochromatic direct photolysis rate constant
 ([mol L⁻¹ d⁻¹], zero-order) of a test chemical exposed to
 monochromatic irradiation at wavelength λ
 $k_{d\lambda(act)(zero\ order)}$ = monochromatic direct photolysis rate constant
 ([mol L⁻¹ d⁻¹], zero-order) of an actinometer exposed to
 monochromatic irradiation at wavelength λ

99. As can be seen from equations 16, 17, and 18, it is not necessary to determine the photon irradiance if monochromatic irradiation is used to determine the test chemical quantum yield. However, it is difficult to relate these results to an environmentally relevant endpoint.

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

100. The quantum yield of an optically dilute test chemical using a low optical density (low decadic absorbance) actinometer and sunlight or a polychromatic filtered xenon arc lamp can be determined from equations 19 and 20, respectively (2) (6) (12):

$$\Phi_{chem} = \Phi_{act} \left(\frac{k_{d(chem)}}{k_{d(act)}} \right) \left(\frac{\sum_{290}^{800} \epsilon_{\lambda(act)} L_{\lambda}}{\sum_{290}^{800} \epsilon_{\lambda(chem)} L_{\lambda}} \right) \quad 19$$

$$\Phi_{chem} = \Phi_{act} \left(\frac{k_{d(chem)}}{k_{d(act)}} \right) \left(\frac{\sum_{290}^{800} \epsilon_{\lambda(act)} I_{0\lambda(xenon)}}{\sum_{290}^{800} \epsilon_{\lambda(chem)} I_{0\lambda(xenon)}} \right) \quad 20$$

where:

Φ_{chem} = the quantum yield of the test chemical
 Φ_{act} = the quantum yield of the actinometer
 $k_{d(chem)}$ = direct photolysis rate constant ([d⁻¹], first order) of the test chemical
 $k_{d(act)}$ = direct photolysis rate constant ([d⁻¹], first order) of the actinometer
 $\epsilon_{\lambda(chem)}$ = molar decadic absorption coefficient of the test chemical [L mol⁻¹ cm⁻¹] at
 wavelength λ
 $\epsilon_{\lambda(act)}$ = molar decadic absorption coefficient of the actinometer [L mol⁻¹cm⁻¹] at
 wavelength λ
 $I_{0\lambda(xenon)}$ = incident filtered xenon arc lamp photon irradiance, on amount basis

$$L_{\lambda} \text{ over} = \frac{[\text{mmol cm}^{-2} \text{ d}^{-1}] \text{ over a 1 nm interval centered at wavelength } \lambda}{\text{average daily solar photon irradiance, on amount basis } [\text{mmol cm}^{-2} \text{ d}^{-1}] \text{ wavelength interval } \Delta\lambda \text{ centered at wavelength } \lambda}$$

101. As can be seen from equations 19 and 20, it is necessary to independently and accurately determine the incident photon irradiance as a function of wavelength in a given wavelength interval when polychromatic irradiation is used to determine the test chemical quantum yield.

102. 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.

Use of the quantum yield to estimate direct photolysis rate constants

103. The first-order rate constant for direct phototransformation and thus the life-time of a test chemical in water can be calculated from the quantum yield (18) (24). Computer programs such as GCSOLAR (18) or ABIWAS (19) (20) can be used to estimate direct photolysis rate constants at any given time (i.e. season), latitude, in near surface water or at any specified water body depths and light attenuation of interest. The programs can also average rate constants over any given time and/or depth interval of interest.

104. 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).

REPORTING OF DATA AND RESULTS

105. The degree of presentation of results depends on the complexity and purpose of the study, that is, the number of tiers. The reporting should follow IUPAC recommendations (36).

Tier 1

- Provide the UV-VISIBLE spectrum or spectra of the test chemical as the molar decadic absorption coefficients [$\text{L mol}^{-1} \text{ cm}^{-1}$] on the y-axis versus wavelengths [nm] on the x-axis.
- Provide tabular values of solar photon irradiances for the season and latitude chosen to estimate maximum photolysis rate constants.
- Report the estimated direct photolysis rate constant under mid-summer irradiance at the surface of a clear natural water and the corresponding half-life. Provide the equations and calculations used to estimate them. Provide the rationale for selecting the season and latitude of the average daily solar photon irradiances (L_{λ}) used in the calculations. Report whether or not the results of the calculations trigger Tier 2.

Tier 2

General Data and results

- If a filtered xenon arc lamp was used, provide the incident photon irradiance in a graph as the photon irradiance [$\text{mmol cm}^{-2} \text{ s}^{-1}$] on the y-axis versus the wavelength [nm] on the x-axis.

- If sunlight was used, provide tabular values of solar photon irradiances for the season and latitude closest to those of the study. In addition report if clouds were present during the irradiation period.
- 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 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 irradiances (L_λ) used in the calculations.

Identification of major transformation products

- Provide table(s) and graph(s) showing the concentrations of the phototransformation products and amount of substance (and optional 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.
- If applicable, report the rate constants for the formation and decline of the transformation products. Report the identity of the major phototransformation products ($\geq 10\%$ on amount basis of the applied dose). Provide the transformation pathway model, equations, calculations, and regression coefficients used to compute them together with regression n and r^2 values, and standard errors of coefficients.

Quantum yields

- If a filtered xenon arc lamp was used, provide the incident photon irradiance in a graph as the photon irradiance [$\text{mmol cm}^{-2} \text{s}^{-1}$] on the y-axis versus the wavelength [nm] on the x-axis.
- If sunlight was used, provide tabular values of solar photon irradiances for the season and latitude closest to those of the study.
- 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 if conducted or if determined after the requirement to report the information for consistency. 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 (e.g. in relation to water depth and suspended and dissolved organic matter content).

Provide and/or describe the equations and calculations or computer program (e.g. GCSOLAR or ABIWAS) and inputs to estimate them.

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 chemical, 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 chemical. As an option, these physical and chemical properties may be listed in a table.
- Report if the test chemical is the primary chemical or any transformation product resulting from abiotic hydrolysis and/or biotransformation. Report if the test chemical is an industrial chemical, a pharmaceutical chemical, a pesticide, etc.
- For radiolabelled test chemicals, 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 chemical. 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 standard deviations for replicate analyses.

Specific experimental information related to photolysis (36)

- 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 its amount of substance fraction used, if any.
 - Nominal and actual concentration of test chemical 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 its amount of substance fraction 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 cutoff, 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
 - Transmission spectrum of filters and their purpose
 - Measured spectrum of the light source between 290 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.
- Quantum Yields:
 - Experimental conditions (temperature, test media, concentration of test chemical 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.
 - 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 chemical
- Computational methods for:
 - Calculation of molar decadic absorption coefficients (ϵ_{λ}) utilizing Beer-Lambert's relationship
 - Maximum photolysis reaction rate assuming $\Phi = 1$
 - Experimental photolysis reaction rate
 - Quantum yield calculations
 - GCSOLAR or ABIWAS calculation of reaction rates at different latitudes, seasons, time of the day, water bodies.
 - Half-lives or DT50, DT75, and DT90 values and appropriate associated confidence intervals.

LITERATURE

1. OECD. OECD Working Group for the Development of a Test Guideline on Phototransformation of Chemicals in Water. Rome, 21-22 September 1998, 1998.
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ANNEX 1

Definitions and Units**General Definitions**

DT50 (Disappearance time 50) is the time within which the concentration of the test chemical is reduced by 0.5 it is different from the half-life $t_{1/2}$ when transformation does not follow first-order kinetics.

DT75 (Disappearance time 75) is the time within which the concentration of the test chemical is reduced by 0.75.

DT90 (Disappearance time 90) is the time within which the concentration of the test chemical is reduced by 0.9.

First-order reaction The rate of a reaction is proportional to the concentration of a reacting single substance. The proportional constant is called the first-order rate constant (unit s^{-1}). The reciprocal of the first-order rate constant is called the lifetime (unit s).

Half-life $t_{1/2}$ is the time taken for 0.5 transformation of a test chemical when the transformation can be described by first-order kinetics; in this case it is independent of concentration.

Lifetime Lifetime of a molecular entity, which decays by first-order kinetics, is the time needed for a concentration of the entity to decrease to $1/e$ of its original value, i.e., $c(t = \tau) = c(t = 0)/e$. Statistically, it represents the life expectation of the entity. It is equal to the reciprocal of the sum of the first-order rate constants of all processes causing the decay of the molecular entity.

Limit of detection (LOD) is the concentration of a substance below which the identity of the substance cannot be distinguished from analytical artefacts.

Limit of quantification (LOQ) is the concentration of a substance below which the concentration cannot be determined with an acceptable accuracy.

Test chemical means any chemical, whether the parent compound or relevant transformation products.

Transformation products refers to all substances resulting from biotic or abiotic transformation reactions of the test chemical including CO_2 .

Zero-order reaction The rate of a reaction is independent of the concentration of the reacting substance(s). The proportional constant is called the zero-order rate constant (unit $mol L^{-1} s^{-1}$).

Photochemical Definitions

The definitions and units thereafter are taken from the Glossary of terms used in photochemistry (IUPAC Recommendations 2006) (11). Commonly used and SI units are provided. Cited with permission from the International Union of Pure and Applied Chemistry.

Decadic Absorbance (A), [without unit] -Logarithm to the base 10 (linear absorbance) of the incident

(prior to absorption) spectral radiant power, P_{λ}^0 divided by the transmitted spectral radiant power, P_{λ}

$$A(\lambda) = \lg \left(\frac{P_{\lambda}^0}{P_{\lambda}} \right) = -\log T(\lambda)$$

In practice, $A(\lambda)$ is the logarithm to the base 10 of the spectral radiant power of ultraviolet, visible, or infrared radiation transmitted through a reference sample divided by that transmitted through the investigated sample, both observed in identical cells. $T(\lambda)$ is the (internal) transmittance at the defined wavelength. 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 .

Actinometer Chemical system for the determination of the number of photons integrally or per time interval absorbed into the defined space of a chemical reactor. This name is commonly applied to systems used in the ultraviolet and visible wavelength ranges. Examples of a chemical actinometer 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. Examples of actinometers are given in Annex 5.

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,

$$A(\lambda) = \lg \left(\frac{P_{\lambda}^0}{P_{\lambda}} \right) = \epsilon(\lambda) \cdot c \cdot l$$

or

$$P_{\lambda} = P_{\lambda}^0 \cdot 10^{-A(\lambda)} = P_{\lambda}^0 \cdot 10^{-\epsilon(\lambda) \cdot c \cdot l}$$

where the proportionality constant, $\epsilon(\lambda)$, is called the molar decadic absorption coefficient and P_{λ}^0 and P_{λ} are, respectively, the incident and transmitted spectral radiant power. For l in cm and c in mol dm^{-3} or M , ϵ will result in $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ or $\text{L mol}^{-1} \text{cm}^{-1}$. These are the commonly used units. The SI unit for ϵ is $\text{m}^2 \text{mol}^{-1}$.

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 (a^{-1}) is the distance at which the spectral radiant power, P_{λ} decreases to one tenth of its incident value, P_{λ}^0 .

Einstein A mole of photons. Widely used, although it is not an SI unit. Einstein sometimes is defined as the energy of one mole of photons. This latter use is discouraged.

Energy Transfer Process by which a molecular entity is excited (e.g., by absorption of ultraviolet, visible, or infrared radiation or by chemiexcitation) and a phenomenon (a physical or a chemical process) originates from the excited state of another molecular entity, which has interacted with the originally absorbing entity. 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.

Fluence (H_0 , F_0), [Jm^{-2}] At a given point in space, the radiant energy, Q , incident on a small sphere from all directions divided by the cross-sectional area of that sphere. The term is used in photochemistry to specify the energy delivered in a given time interval (e.g., by a laser pulse).

Frequency (ν or ω), [s^{-1} or $rad\ s^{-1}$] 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.

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

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

Irradiance (E), [Wm^{-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). 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. $E = \int_{\lambda} E_{\lambda} d\lambda$, where E_{λ} is the spectral irradiance at wavelength λ .

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

Lamp A source of incoherent radiation.

Merry-Go-Round Reactor, Turntable Reactor Apparatus in which several samples are rotated around a radiation source in order to expose each to equal amounts of radiation.

Molar Decadic Absorption Coefficient, [$dm^3\ mol^{-1}\ cm^{-1}$, $L\ mol^{-1}\ cm^{-1}$] Decadic absorbance divided by the absorption pathlength, l , and the concentration, c :

$$\epsilon(\lambda) = \frac{1}{c \cdot l} \cdot \lg \frac{P^0_{\lambda}}{P_{\lambda}} = \frac{A(\lambda)}{c \cdot l}$$

where P^0_{λ} and P_{λ} are, respectively, the incident and transmitted spectral radiant power. The term molar decadic absorptivity for molar decadic absorption coefficient should be avoided. In common usage for l/cm and $c/mol\ dm^{-3}$, $\epsilon(\lambda)$ results in $dm^3\ mol^{-1}\ cm^{-1}$ ($L\ mol^{-1}\ cm^{-1}$, the most commonly used unit), which equals $0.1\ m^2\ mol^{-1}$ (coherent SI units).

Optical Bench An apparatus for observation and measurement of optical phenomena (definition not taken from (11)). In (12) an optical bench for photochemical experiments is termed a "photochemical optical bench" (POB).

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

Photochemistry Branch of chemistry concerned with the chemical effects of ultraviolet, visible, or infrared radiation.

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

Photolysis Bond cleavage induced by ultraviolet, visible, or infrared radiation. Term often used incorrectly to describe irradiation of a sample, although in the combination flash photolysis this usage is accepted.

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).

Photon Flux (q_p), [s^{-1}] Number of photons (quanta of radiation, N_p) per time interval.

Photon Irradiance (E_p), [$m^{-2} s^{-1}$] Number of photons (quanta of radiation, N_p) per time interval (photon flux), q_p , incident from all upward directions on a small element of surface containing the point under consideration divided by the area of the element. This quantity can be used on a chemical amount basis by dividing E_p by the Avogadro constant, the symbol then being $E_{n,p}$, the name "photon irradiance, amount basis", SI unit is $mol m^{-2} s^{-1}$; common unit is einstein $m^{-2} s^{-1}$.

Photooxidation Reactions induced by light. Common process are:

- The loss of one or more electrons from a chemical species as a result of photoexcitation 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) 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:

$$\Phi(\lambda) = \frac{\text{number of events}}{\text{number of photons absorbed}}$$

For a photochemical reaction,

$$\Phi(\lambda) = \frac{\text{amount of reactant consumed or product formed}}{\text{amount of photons absorbed}}$$

The differential quantum yield is

$$\Phi(\lambda) = \frac{dx/dt}{q_{n,p}^0 \cdot (1 - 10^{-A(\lambda)})}$$

where dx/dt is the rate of change of a measurable quantity (spectral or any other property), and $q_{n,p}^0$ the amount of photons (mol or its equivalent einstein) incident (prior to absorption) per time interval (photon flux, amount basis). $A(\lambda)$ is the decadic absorbance at the excitation wavelength. Strictly, the term quantum yield applies only for monochromatic excitation. 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 ($Q = \int_{\lambda} Q_{\lambda} d\lambda$). 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), [Jm^{-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 Power (P), [Js^{-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 $^1\Sigma g^+$. Use of the term "singlet oxygen" alone, without mention of the chemical species is discouraged since it can also refer to an oxygen atom in a 1S or 1D excited state.

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 Photon Flux ($q_{p,\lambda}$), [$s^{-1} m^{-1}$ or $s^{-1} nm^{-1}$] Derivative of photon flux, number basis, q_p , with respect to wavelength, λ . This quantity can be expressed on a chemical amount basis by dividing $q_{p,\lambda}$, by the Avogadro constant, the name then is "spectral photon flux, amount basis", the symbol $q_{n,p,\lambda}$ and the SI unit is $mol s^{-1} m^{-1}$; common unit is einstein $s^{-1} nm^{-1}$.

Spectral Photon Irradiance ($E_{p,\lambda}$), [$s^{-1} m^{-3}$ or $s^{-1} cm^{-2} nm^{-1}$] Derivative of photon irradiance, E_p , with respect to wavelength, λ . This quantity can be expressed on a chemical amount basis by dividing $E_{p,\lambda}$, by the Avogadro constant, the name then is "spectral photon irradiance, amount basis", the symbol $E_{n,p,\lambda}$, and the SI unit is $mol s^{-1} m^{-3}$; common unit is einstein $s^{-1} m^{-2} nm^{-1}$.

Spectral Irradiance (E_λ), [Wm^{-3} , or $Wm^{-2} nm^{-1}$] Derivative of irradiance, E , with respect to wavelength, λ .

Triplet State A state having a total electron 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

Table 1: Symbols and units related to photochemistry with their SI unit and commonly used units

Symbol	Name	SI Units	Common Units
A	Absorbance	without unit	without unit
a	Decadic absorption coefficient	m ⁻¹	cm ⁻¹
D	Attenuance	without unit	without unit
E	Irradiance	W m ⁻²	W cm ⁻²
E ₀	Fluence rate	W m ⁻²	
E _p	Photon Irradiance, on amount basis	mol s ⁻¹ m ⁻²	mol s ⁻¹ cm ⁻²
E _{p,λ}	Spectral Photon Irradiance, on amount basis	mol s ⁻¹ m ⁻³	mol s ⁻¹ cm ⁻² nm ⁻¹
ε	Molar decadic absorption coefficient	m ² mol ⁻¹	dm ³ mol ⁻¹ cm ⁻¹ or L mol ⁻¹ cm ⁻¹
Φ	Quantum yield	without unit	without unit
H	Radiant exposure	J m ⁻²	
H ₀	Fluence	J m ⁻²	
λ	Wavelength	m	nm
ν; σ	Wavenumber	m ⁻¹	cm ⁻¹
P	Radiant Power	W = J s ⁻¹	
Q	Radiant energy	J	

Note:

Photon Irradiance

The symbol I_{λ} was used in this guideline for the "Photon Irradiance" without exception on an amount basis. For a chemical exposed to polychromatic irradiation by a number of photons over a 1 nm interval centered at wavelength λ , $I_{0\lambda}$ is used with the unit mmol cm⁻² s⁻¹.

Average Daily Solar Photon Irradiance

The symbol L_{λ} was used in this guideline for the "Average Daily Solar Photon Irradiance" without exception on an amount basis. For a chemical exposed to sunlight (a polychromatic light source) over a wavelength interval $\Delta\lambda$ centered at wavelength λ , L_{λ} is used with the unit mmol cm⁻² d⁻¹.

ANNEX 3

Derivations of Selected Equations

Background equations (12):

$$\left(\frac{dc}{dt}\right)_\lambda = -\Phi \cdot I_{\lambda(\text{abs by chem})} = -\frac{\Phi}{D_{\text{sys}}} \cdot I_{0\lambda} \cdot F_{\lambda(\text{abs by sys})} \cdot F_{\lambda(\text{abs by chem})} \quad 3-1$$

$$\frac{dc}{dt} = -\Phi \sum_{290}^{800} I_{\lambda(\text{abs by chem})} = -\frac{\Phi}{D_{\text{sys}}} \sum_{290}^{800} I_{0\lambda} \cdot F_{\lambda(\text{abs by sys})} \cdot F_{\lambda(\text{abs by chem})} \quad 3-2$$

where:

- c = concentration of chemical [mol L⁻¹]
- Φ = quantum yield
- I_{λ(abs by chem)} = photon absorption rate by the chemical over a 1 nm interval centered at wavelength λ [mmol cm⁻³ d⁻¹]
- D_{sys} = depth of irradiated system [cm] = volume of irradiated system/incident area
- I_{0λ} = incident photon irradiance over a 1 nm interval centered at wavelength λ [mmol cm⁻² d⁻¹]
- F_{λ(abs by sys)} = fraction of incident photon irradiance absorbed by the system
- F_{λ(abs by chem)} = fraction of incident photon irradiance absorbed by the chemical

$$F_{\lambda(\text{abs by sys})} = \frac{I_{0\lambda} - I_{t\lambda}}{I_{0\lambda}} = \frac{I_{0\lambda} (1 - 10^{-(\alpha_\lambda + \epsilon_\lambda c) l})}{I_{0\lambda}} = 1 - 10^{-(\alpha_\lambda + \epsilon_\lambda c) l} \quad 3-3$$

$$F_{\lambda(\text{abs by chem})} = \frac{\epsilon_\lambda \cdot c}{\alpha_\lambda + \epsilon_\lambda \cdot c} \quad 3-4$$

where:

- α_λ = attenuation coefficient of the system at wavelength λ [cm⁻¹]
- ε_λ = molar decadic absorption coefficient of the chemical at wavelength λ [L mol⁻¹ cm⁻¹]
- l = light pathlength [cm]

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

$$\left(\frac{dc}{dt}\right)_\lambda = -\frac{\Phi}{D_{\text{sys}}} \cdot I_{0\lambda} \cdot \left(1 - 10^{-(\alpha_\lambda + \epsilon_\lambda c) l}\right) \cdot \left(\frac{\epsilon_\lambda \cdot c}{\alpha_\lambda + \epsilon_\lambda \cdot c}\right) \quad 3-5$$

Summing equation 3-5 over all wavelengths from 290 nm to 800 nm gives:

$$\frac{dc}{dt} = -\frac{\Phi}{D_{sys}} \sum_{290}^{800} \left[I_{0\lambda} \cdot \left(1 - 10^{-(\alpha_\lambda + \epsilon_\lambda c) l} \right) \cdot \left(\frac{\epsilon_\lambda \cdot c}{\alpha_\lambda + \epsilon_\lambda \cdot c} \right) \right] \quad 3-6$$

For solar irradiation on an aqueous system (12),

$$I_{0\lambda(solar)}(t) = I_{d\lambda}(t) + I_{s\lambda}(t) \quad 3-7$$

$$\bar{l}_d \cong D_{sys} \cdot \sec \theta(t) \quad 3-8$$

$$\bar{l}_s = 1.2 \cdot D_{sys} \quad 3-9$$

where:

- $I_{0\lambda(solar)}(t)$ = total incident solar photon irradiance as a function of time
- $I_{d\lambda}(t)$ = direct incident solar photon irradiance as a function of time
- $I_{s\lambda}(t)$ = sky radiation incident solar photon irradiance as a function of time
- \bar{l}_d = average light pathlength for direct irradiation [cm]
- \bar{l}_s = average light pathlength for sky irradiation [cm]
- $\theta(t)$ = angle of reflection

$$\frac{dc}{dt} = -\frac{\Phi}{D_{sys}} \sum_{290}^{800} \left[\left\{ I_{d\lambda} \cdot \left(1 - 10^{-(\alpha_\lambda + \epsilon_\lambda c) D_{sys} \sec \theta} \right) + I_{s\lambda} \cdot \left(1 - 10^{-(\alpha_\lambda + \epsilon_\lambda c) 1.2 D_{sys}} \right) \right\} \cdot \left(\frac{\epsilon_\lambda \cdot c}{\alpha_\lambda + \epsilon_\lambda \cdot c} \right) \right] \quad 3-10$$

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

$$10^{-x} = \exp(-2.3 \cdot x) \quad 3-11$$

Therefore:

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

where:

$$x = 2.3 \cdot (\alpha_\lambda + \epsilon_\lambda c) l = 2.3 \cdot A \quad 3-13$$

- A = decadic absorbance of the solution

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

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

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 decadic 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:

$$1 - \exp(-x) \cong x \quad 3-15$$

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:

$$1 - 10^{-(\alpha_\lambda + \epsilon_\lambda c) l} = 2.3 \cdot (\alpha_\lambda + \epsilon_\lambda c) l \quad 3-16$$

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:

$$\frac{dc}{dt} = - \left(2.3 \cdot \frac{l}{D_{sys}} \Phi \sum_{290}^{800} \epsilon_\lambda I_{0\lambda} \right) c \quad 3-17$$

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:

$$k_d = 2.3 \cdot \frac{l}{D_{sys}} \Phi \sum_{290}^{800} \epsilon_\lambda I_{0\lambda} \quad 3-18$$

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 decadic absorbance of the system is < 0.02 ,

$$1 - 10^{-(\alpha_\lambda + \epsilon_\lambda c) D_{sys} \sec \theta} \cong 2.3 \cdot (\alpha_\lambda + \epsilon_\lambda c) D_{sys} \sec \theta \quad 3-19$$

$$1 - 10^{-(\alpha_\lambda + \epsilon_\lambda c) 1.2 D_{sys}} \cong 2.3 \cdot (\alpha_\lambda + \epsilon_\lambda c) 1.2 D_{sys} \quad 3-20$$

Substituting equations 3-19 and 3-20 into equation 1 and canceling out the resulting identical terms in the numerator and denominator gives:

$$\frac{dc}{dt} = - \left(2.3 \Phi \sum_{290}^{800} \epsilon_\lambda Z_\lambda(t) \right) \cdot c \quad 3-21$$

where:

$$Z_\lambda(t) = I_{d\lambda}(t) \cdot \sec \theta + 1.2 I_{s\lambda}(t) \quad 3-22$$

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

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

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

$$L_{\lambda} = 2.3 \cdot \overline{Z_{\lambda}} \quad 3-24$$

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

$$\overline{\left(\frac{dc}{dt}\right)} = - \left(\Phi \sum_{290}^{800} \epsilon_{\lambda} L_{\lambda} \right) \cdot c \quad 3-25$$

By comparing equation 3-24 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:

$$\overline{k_{d(solar)}} = \Phi \sum_{290}^{800} \epsilon_{\lambda} L_{\lambda} \quad 3-26$$

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

Derivation of equation 7 in the main text

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

$$I_{(abs \text{ by chem})} = \sum_{290}^{800} I_{\lambda(abs \text{ by chem})} = -\frac{1}{\Phi} \frac{dc}{dt} \quad 3-27$$

where:

$I_{(abs \text{ by chem})}$ = total photon absorption rate by the chemical [$\text{mmol cm}^{-3} \text{ d}^{-1}$]
 $I_{\lambda(abs \text{ by chem})}$ = photon absorption rate by the chemical over a 1 nm interval centered at wavelength λ [$\text{mmol cm}^{-3} \text{ d}^{-1}$]

Multiplying equations 3-17 and 3-25 by $-1/\Phi$ gives the total photon absorption rate by the test chemical in an optically dilute solution exposed to xenon arc lamp or solar irradiation, respectively:

$$I_{(xenon \text{ abs by chem})} = \left(2.3 \frac{l}{D_{sys}} \sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda(xenon)} \right) \cdot c_{xenon} \quad 3-28$$

$$I_{(solar \text{ abs by chem})} = \left(\sum_{290}^{800} \epsilon_{\lambda} L_{\lambda} \right) \cdot c_{solar} \quad 3-29$$

The total number of photons absorbed by a test chemical in a low optical density solution over X days of xenon arc lamp irradiation or over 30 days of solar irradiation are given respectively by:

$$\frac{\text{Total number of photons abs by chem}}{cm^3} = \text{(X days xenon)} \left(2.3 \frac{l}{D_{sys}} \sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda}(\text{xenon}) \right) \cdot \overline{c_{\text{xenon}}} \quad 3-30$$

$$\frac{\text{Total number of photons abs by chem}}{cm^3} = \text{(30 days solar)} \left(\sum_{290}^{800} \epsilon_{\lambda} L_{\lambda} \right) \cdot \overline{c_{\text{solar}}} \quad 3-31$$

The number of days (X) of constant irradiation by a filtered xenon arc lamp that is equivalent to 30 days of solar irradiation of a low (decadic) absorbance water can be obtained by equating equations 3-30 and 3-31, assuming that the average concentration over 30 days of solar irradiation ($\overline{c_{\text{solar}}}$) is equal to the average concentration over X days of constant irradiation by a xenon arc lamp ($\overline{c_{\text{xenon}}}$), solving for X and substituting D_{cell} for D_{sys} :

$$\text{X days xenon} = \left(\frac{30}{2.3} \frac{D_{\text{cell}}}{l} \right) \frac{\sum_{290}^{800} \epsilon_{\lambda} L_{\lambda}}{\sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda}(\text{xenon})} = \left(13 \frac{D_{\text{sys}}}{l} \right) \frac{\sum_{290}^{800} \epsilon_{\lambda} L_{\lambda}}{\sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda}(\text{xenon})} \quad 3-32$$

where equation 3-32 is identical to equation 7 in the main text.

Derivation of equation 12 in the main text

Dividing equation 3-26 (for the first-order rate constant of a test chemical in an optically dilute solution exposed to sunlight) by equation 3-18 (for the first-order rate constant of a test chemical in an optically dilute solution exposed to a filtered xenon arc lamp, i.e. $k_d = k_{d(\text{xenon})}$, $I_{0\lambda} = I_{0\lambda(\text{xenon})}$, and $D_{\text{sys}} = D_{\text{cell}}$) and rearranging gives:

$$k_{d(\text{solar})} = \frac{1}{2.3} \cdot \frac{D_{\text{cell}}}{l} \frac{k_{d(\text{xenon})} \sum_{290}^{800} \epsilon_{\lambda} L_{\lambda}}{\sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda(\text{xenon})}} \quad 3-33$$

where equation 3-33 is identical to equation 12 in the main text.

ANNEX 4

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 $\text{NaH}_2\text{PO}_4/\text{HCl}$
- For pHs in the range of 6 to 8, use $\text{KH}_2\text{PO}_4/\text{NaOH}$
- For pHs in the range of 8 to 10, use $\text{H}_3\text{BO}_3/\text{NaOH}$
- 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 (at least $0.0025 \text{ mol L}^{-1}$).

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 $1 \text{ mol L}^{-1} \text{ HCl}$ 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.

ANNEX 5

Advantages and Disadvantages of Monochromatic and Polychromatic Irradiation

1. The main advantage in using monochromatic irradiation to determine the quantum yield of the test chemical is that it eliminates the need to directly measure the incident monochromatic irradiation (see equations 16 through 18 in the main text). 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 irradiances at just one wavelength instead of over multiple wavelengths.

2. 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 irradiances 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 (see equations 19 and 20 in the main text), its use requires the determination of the photon irradiance.

3. 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 irradiance caused by fog, varying cloud cover, etc. (12) (33).

4. An example of an adjustable quantum yield actinometer is the p-nitroacetophenone - pyridine (PNAP-PYR) actinometer (37). For a $1.0 \cdot 10^{-5}$ mol L⁻¹ 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):

$$\Phi_{act} = 0.0169 \cdot c(\text{pyridine}) \quad 5-1$$

where:

Φ_{act} = quantum yield of the $1.0 \cdot 10^{-5}$ mol L⁻¹ p-nitroacetophenone
 $c(\text{pyridine})$ = molar concentration of pyridine

5. Suitable chemical actinometers used in aqueous photochemical studies are summarized in Table 2.

Table 2: Suitable actinometer (systems). $\Delta\lambda/\text{nm}$ = optimal wavelength range for their use taken from (12), (28); Φ (solvent) = quantum yield Φ of the actinometer taken from (12), (28) in the usual solvent (a quantum yield independent from wavelength is abbreviated as $\Phi(\lambda)=\text{const}$); Literature = exemplary references of typical applications.

	Actinometer System	$\Delta\lambda/\text{nm}$	Φ (solvent)	Literature
(a)	p-nitroacetophenone/pyridine	290-370	variable, $\Phi(\lambda)=\text{const}$ (water, 1% CH_3CN)	(37) (37)
(b)	p-nitroanisole/pyridine	290-370	variable, $\Phi(\lambda)=\text{const}$ (water, 1% CH_3CN)	(38) (37)
(c)	valerophenone	290-330	$\sim 0.98\pm 0.04$ (water)	(39) (39)
(d)	ferrioxalate	250-500	1.25-0.9 (water)	(40), (41), (21) (34), (42), (43)
(e)	o-nitrobenzaldehyde	300-410	0.5 (acetone or CH_2Cl_2)	(21) (37)
(f)	Reinecke's salt	316-750	~ 0.3 (water)	(12)
(g)	aberchrome 540	310-375	0.2 (toluene)	(44) (45)
(h)	azobenzene	230-460	$\Phi(\text{trans}\rightarrow\text{cis})=0.14$ $\Phi(\text{cis}\rightarrow\text{trans})=0.48$ (methanol)	(46) (47)
(i)	oxalic acid/uranyl sulphate	200-500	0.5-0.6 (0.1 mol/L H_2SO_4)	(8)

6. The first two actinometers listed in Table 2 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 six are high optical density actinometers. Other chemical actinometers are described in the IUPAC document on chemical actinometers (28).

ANNEX 6

Experimental setups

Many different experimental setups were published to investigate photolysis reactions in solution. A commonly used configuration is the "merry-go-round" photochemical reactor. The first original publication from Moses (48) already describes the detailed setup, technical sketches can be found in (42), and a general discussion of the application of a "merry-go-round" apparatus in photolysis studies can be found in (12) (42). Merry-go-round photochemical reactors are commercially available (31) (32) and an apparatus used in practice is shown in Figure 2.

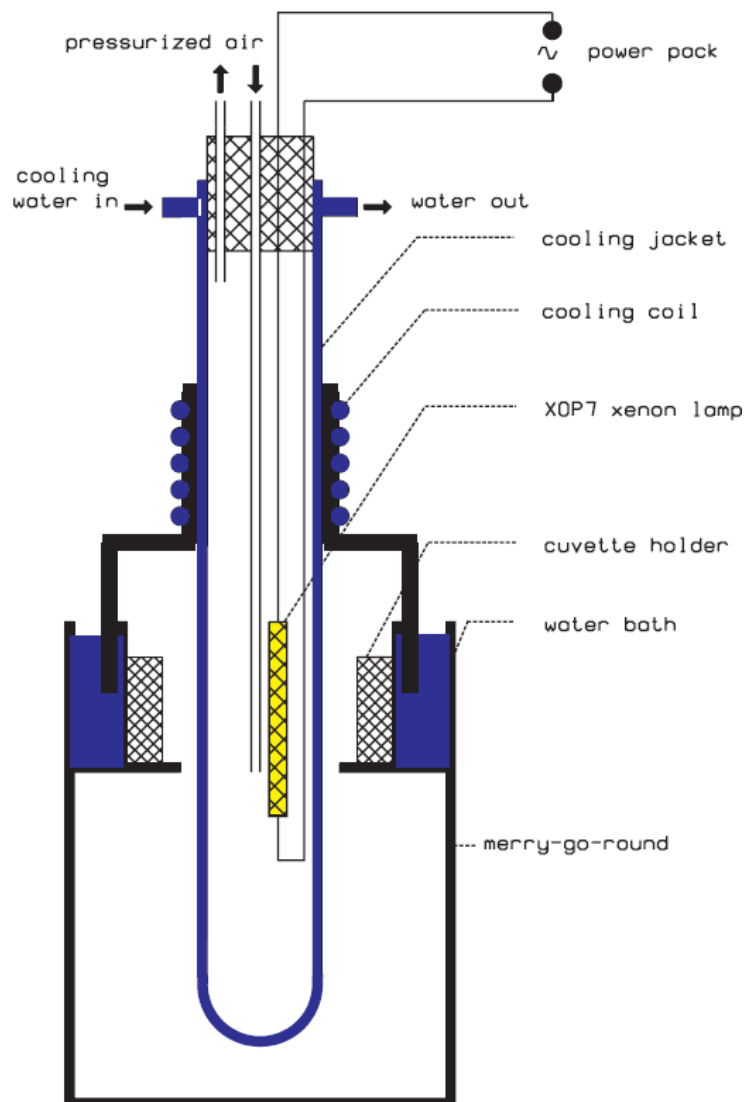


Figure 2: A typical "merry-go-round" apparatus for the parallel photolysis of up to 10 cuvettes ($l=1$ cm, $V=3.5$ cm³) using a xenon-light source.

The second most common apparatus in photolysis studies is an "Optical Bench". The principle setup of an optical bench is for instance discussed in (12) and an example is shown in Figure 3. Further examples used in photolysis experiments in solution include setups for uniform irradiances using xenon light sources (30) (31), flow-through systems (24) and setups to trap

volatiles (27) (49). A "suntest" apparatus capable to photolyze also large volumes is shown in Figure 4. Numerous designs from different companies of this type of irradiation apparatus are on the market.

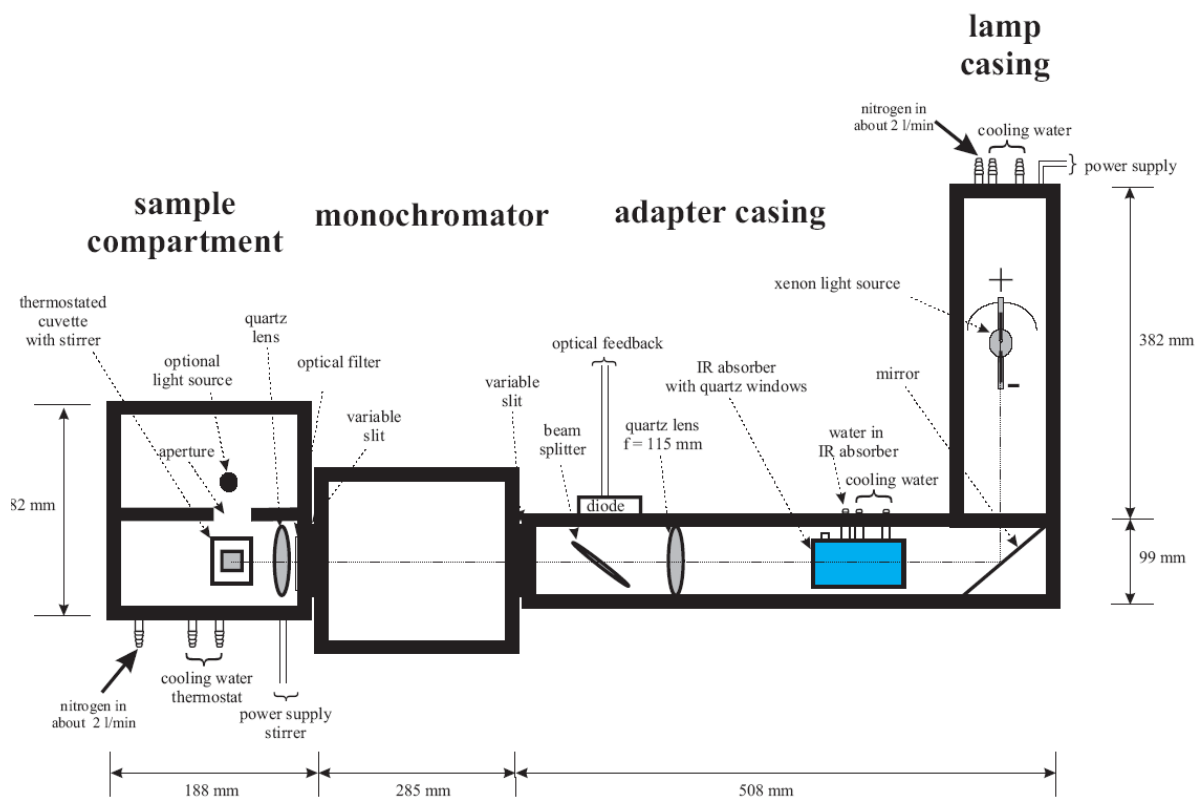


Figure 3: Scheme of an "Optical Bench" to investigate wavelength resolved photolysis reactions using a monochromator.

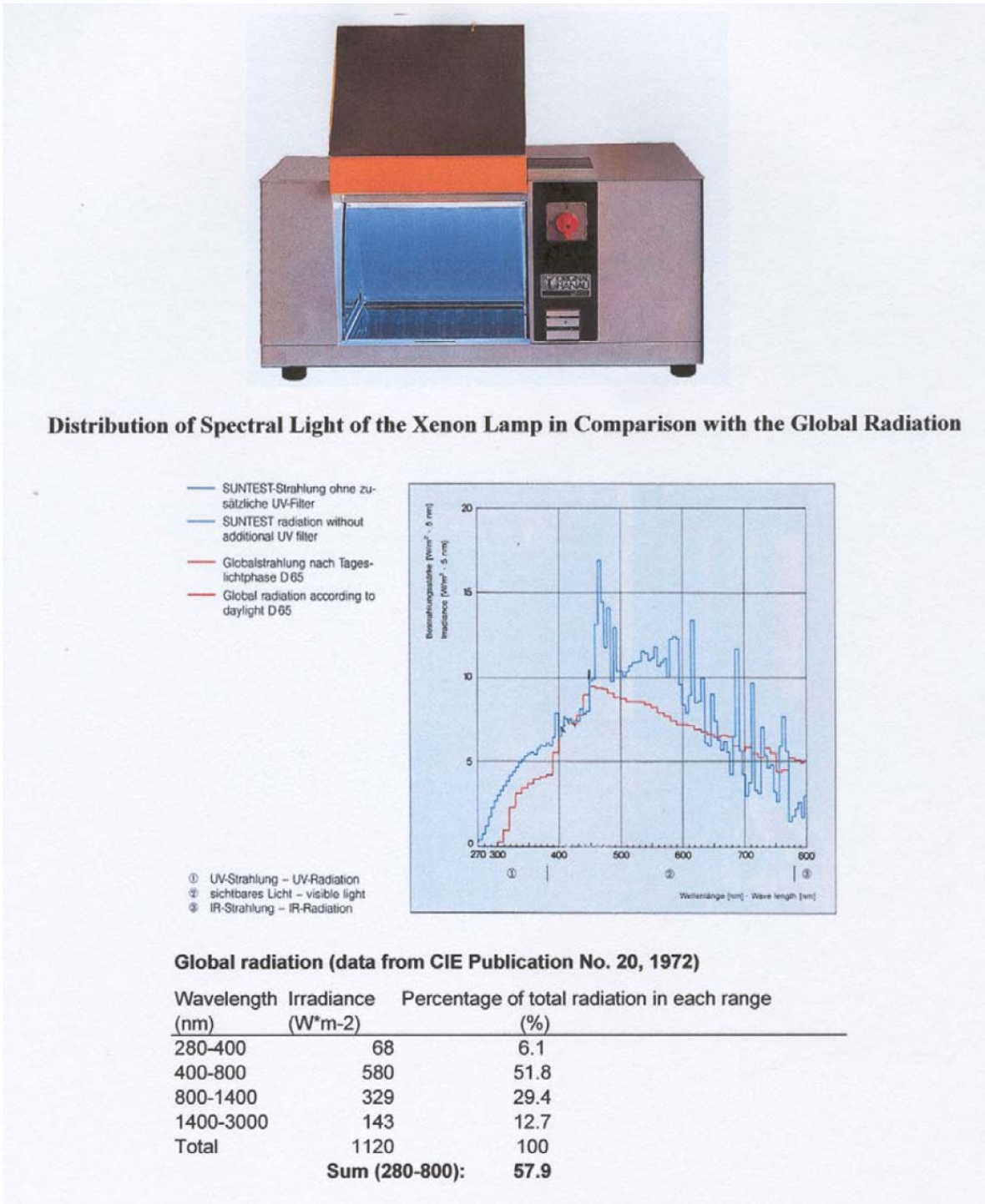


Figure 4: A "Suntest" apparatus (Heraeus, Hanau, Germany) to investigate photolysis reactions using a xenon lamp as polychromatic light source.

ANNEX 7

Examples

Illustrative examples of maximum direct photolysis rates $k_{d(\max)}$ (equation 10), photoreactions of the test chemical, determination of quantum yields using artificial light sources and sunlight are already available in (2) (12) (17) (18).

Example for Tier 1: Estimation of the maximum possible direct photolysis rate constant

Maximum possible direct photolysis rate constants $k_{d(\max)}$ (equation 10) for four test chemicals used in a region at latitude 40° with known highest concentrations in the environment in summer need to be estimated. Average daily solar photon irradiances (L_λ) for different seasons and latitudes can be found for instance in (2) (12) (18). As example values of L_λ at 40° latitude for summer for $\lambda = 297.5 - 380$ nm were taken from (2) and tabulated in Table 3.

Table 3: Wavelengths and average daily solar photon irradiances (L_λ) (on amount basis, taken from (2)) for the wavelength interval $\Delta\lambda$ at 40° latitude for the summer season. L_λ below 296.2 nm (start wavelength of the first wavelength interval) is zero and not shown.

Wavelength and intervals				Daily solar photon irradiance
λ_{center} nm	λ_{start} nm	λ_{end} nm	$\Delta\lambda$ nm	L_λ (on amount basis) $\text{mmol cm}^{-2} \text{d}^{-1}$
297.5	296.2	298.7	2.5	$6.17 \cdot 10^{-5}$
300.0	298.7	301.2	2.5	$2.70 \cdot 10^{-4}$
302.5	301.2	303.7	2.5	$8.30 \cdot 10^{-4}$
305.0	303.7	306.2	2.5	$1.95 \cdot 10^{-3}$
307.5	306.2	308.7	2.5	$3.74 \cdot 10^{-3}$
310.0	308.7	311.2	2.5	$6.17 \cdot 10^{-3}$
312.5	311.2	313.7	2.5	$9.07 \cdot 10^{-3}$
315.0	313.7	316.2	2.5	$1.22 \cdot 10^{-2}$
317.5	316.2	318.7	2.5	$1.55 \cdot 10^{-2}$
320.0	318.7	321.2	2.5	$1.87 \cdot 10^{-2}$
323.1	321.2	325.0	3.8	$3.35 \cdot 10^{-2}$
330.0	325.0	335.0	10.0	$1.16 \cdot 10^{-1}$
340.0	335.0	345.0	10.0	$1.46 \cdot 10^{-1}$
350.0	345.0	355.0	10.0	$1.62 \cdot 10^{-1}$
360.0	355.0	365.0	10.0	$1.79 \cdot 10^{-1}$
370.0	365.0	375.0	10.0	$1.91 \cdot 10^{-1}$
380.0	375.0	385.0	10.0	$2.04 \cdot 10^{-1}$

Mean values of molar decadic absorption coefficients $\epsilon_{\lambda(\text{chem})}$ of the four test chemicals A-D for the corresponding wavelength intervals summarized in Table 3 are shown in Table 4.

Table 4: Wavelength, average daily solar photon irradiances (L_λ) (40° latitude, summer, see Table 3), molar decadic absorption coefficients $\varepsilon_{\lambda(\text{chem})}$, and the corresponding product $L_\lambda \cdot \varepsilon_{\lambda(\text{chem})}$ of 4 test chemicals A-D.

λ_{center} nm	L_λ mmol cm ⁻² d ⁻¹	$\varepsilon_{\lambda(\text{chem})} / \text{L mol}^{-1} \text{ cm}^{-1}$				$L_\lambda \varepsilon_{\lambda(\text{chem})} / \text{d}^{-1}$			
		A	B	C	D	A	B	C	D
297.5	$6.17 \cdot 10^{-5}$	0	15	430	10600	0	$9.26 \cdot 10^{-4}$	$2.65 \cdot 10^{-2}$	$6.55 \cdot 10^{-1}$
300.0	$2.70 \cdot 10^{-4}$	0	5	210	11100	0	$1.35 \cdot 10^{-3}$	$5.67 \cdot 10^{-2}$	$2.98 \cdot 10^0$
302.5	$8.30 \cdot 10^{-4}$	0	1	100	11200	0	$8.30 \cdot 10^{-4}$	$8.30 \cdot 10^{-2}$	$9.33 \cdot 10^0$
305.0	$1.95 \cdot 10^{-3}$	0	0	50	11400	0	0	$9.75 \cdot 10^{-2}$	$2.23 \cdot 10^1$
307.5	$3.74 \cdot 10^{-3}$	0	0	30	11400	0	0	$1.12 \cdot 10^{-1}$	$4.28 \cdot 10^1$
310.0	$6.17 \cdot 10^{-3}$	0	0	20	11200	0	0	$1.23 \cdot 10^{-1}$	$6.92 \cdot 10^1$
312.5	$9.07 \cdot 10^{-3}$	0	0	5	11000	0	0	$4.54 \cdot 10^{-2}$	$1.00 \cdot 10^2$
315.0	$1.22 \cdot 10^{-2}$	0	0	0	10500	0	0	0	$1.28 \cdot 10^2$
317.5	$1.55 \cdot 10^{-2}$	0	0	0	9890	0	0	0	$1.53 \cdot 10^2$
320.0	$1.87 \cdot 10^{-2}$	0	0	0	9380	0	0	0	$1.75 \cdot 10^2$
323.1	$3.35 \cdot 10^{-2}$	0	0	0	8480	0	0	0	$2.84 \cdot 10^2$
330.0	$1.16 \cdot 10^{-1}$	0	0	0	6200	0	0	0	$7.19 \cdot 10^2$
340.0	$1.46 \cdot 10^{-1}$	0	0	0	3050	0	0	0	$4.46 \cdot 10^2$
350.0	$1.62 \cdot 10^{-1}$	0	0	0	960	0	0	0	$1.56 \cdot 10^2$
360.0	$1.79 \cdot 10^{-1}$	0	0	0	179	0	0	0	$3.20 \cdot 10^1$
370.0	$1.91 \cdot 10^{-1}$	0	0	0	24	0	0	0	$4.58 \cdot 10^0$
380.0	$2.04 \cdot 10^{-1}$	0	0	0	5	0	0	0	$1.02 \cdot 10^0$
sum of columns = $k_{d(\text{max})} / \text{d}^{-1} \rightarrow$						0	$3.11 \cdot 10^{-3}$	$5.45 \cdot 10^{-1}$	$2.35 \cdot 10^3$

The maximum value of the solar photolysis rate constant $k_{d(\text{max})}$ (equation 10) is obtained with $\Phi = 1$ from $k_{d(\text{solar})}$ in equation 6. Summation in equation 6 and 10 needs to be performed from $\lambda_{\text{initial}} = 290 \text{ nm}$ to $\lambda_{\text{final}} = 800 \text{ nm}$. In the case of the data presented in Table 3 and 4 the initial wavelength is $\lambda_{\text{initial}} = 296.2 \text{ nm}$ (wavelength interval $\Delta\lambda = 2.5 \text{ nm}$, centered at 297.5 nm), defined by the daily solar photon irradiances L_λ ($L_\lambda = 0$ for $\lambda < 296.2 \text{ nm}$). The final wavelength is $\lambda_{\text{final}} = 385 \text{ nm}$ (wavelength interval $\Delta\lambda = 10 \text{ nm}$, centered at 380 nm), defined by the absorption spectrum ($\varepsilon_{\lambda(\text{D})}$) of test chemical D ($\varepsilon_{\lambda(\text{D})} = 0$ for $\lambda > 385 \text{ nm}$).

- Test chemical A should serve as the trivial example of a compound with molar decadic absorption coefficients $\varepsilon_{\lambda(\text{chem})} = 0$ for $\lambda \geq 290 \text{ nm}$.
- Test chemical B should serve as an example of a compound with (hypothetical) molar decadic absorption coefficients $\varepsilon_{\lambda(\text{chem})} > 10$ above the 290 nm cutoff of solar irradiation at the earth's surface, satisfying the criterium in paragraph 67.
- Test chemical C should serve as an example of a compound with a weak absorption below 314 nm.

- Test chemical D should serve as an example of a compound with strong absorption below 400 nm

Necessary products $L_{\lambda} \cdot \varepsilon_{\lambda(\text{chem})}$ (see equation 10) of test chemicals A-D are given in Table 4. Maximum possible direct photolysis rate constants $k_{d(\text{max})}$ (which are defined as the sum of $L_{\lambda} \cdot \varepsilon_{\lambda(\text{chem})} / \text{d}^{-1}$, see Table 4), half-lives (equation 4) used as a trigger value for Tier 2 and the corresponding decisions are summarized in Table 5 for test chemicals A-D.

Table 5: Estimated maximum possible direct photolysis rate constants for the four test chemicals A-D, half-lives used as a trigger value for Tier 2 and the corresponding decision.

Value	Test Chemical			
	A	B	C	D
$k_{d(\text{max})} / \text{d}^{-1}$	0	$3.11 \cdot 10^{-3}$	$5.45 \cdot 10^{-1}$	$2.35 \cdot 10^3$
$t_{1/2} / \text{d}$	∞	222	1.3	0.00030
Decision	Direct photolysis negligible		Direct photolysis possible Go to higher tier	

Example for Tier 2: Experimental study

Test chemical C was photolyzed in a thermostated "merry-go-round" ($T=25\text{ }^{\circ}\text{C}$) with a xenon-light source in stoppered quartz cuvettes (light pathlength $l=1\text{ cm}$, $V=3.5\text{ ml}$) for 18 hours. Ten cuvettes were used and after 2 hours irradiation time a cuvette was removed and test chemical C was analyzed, respectively. Start concentration of test chemical C was $c_0 = 1 \cdot 10^{-5}\text{ mol L}^{-1}$ in a filtered ($0.45\text{ }\mu\text{m}$) aqueous solution equilibrated for some days in the laboratory and thereby saturated with air at the beginning of the study at $T = 25\text{ }^{\circ}\text{C}$. Analysis was performed by HPLC without any clean-up steps or enrichment using directly 1 ml of the solution, respectively. In parallel a vessel with the same solution used in the photolysis experiment was wrapped with aluminum foil and stored in the dark at $T=25\text{ }^{\circ}\text{C}$. This solution served as dark control and was analyzed accordingly. Concentrations obtained are shown in Figure 5.

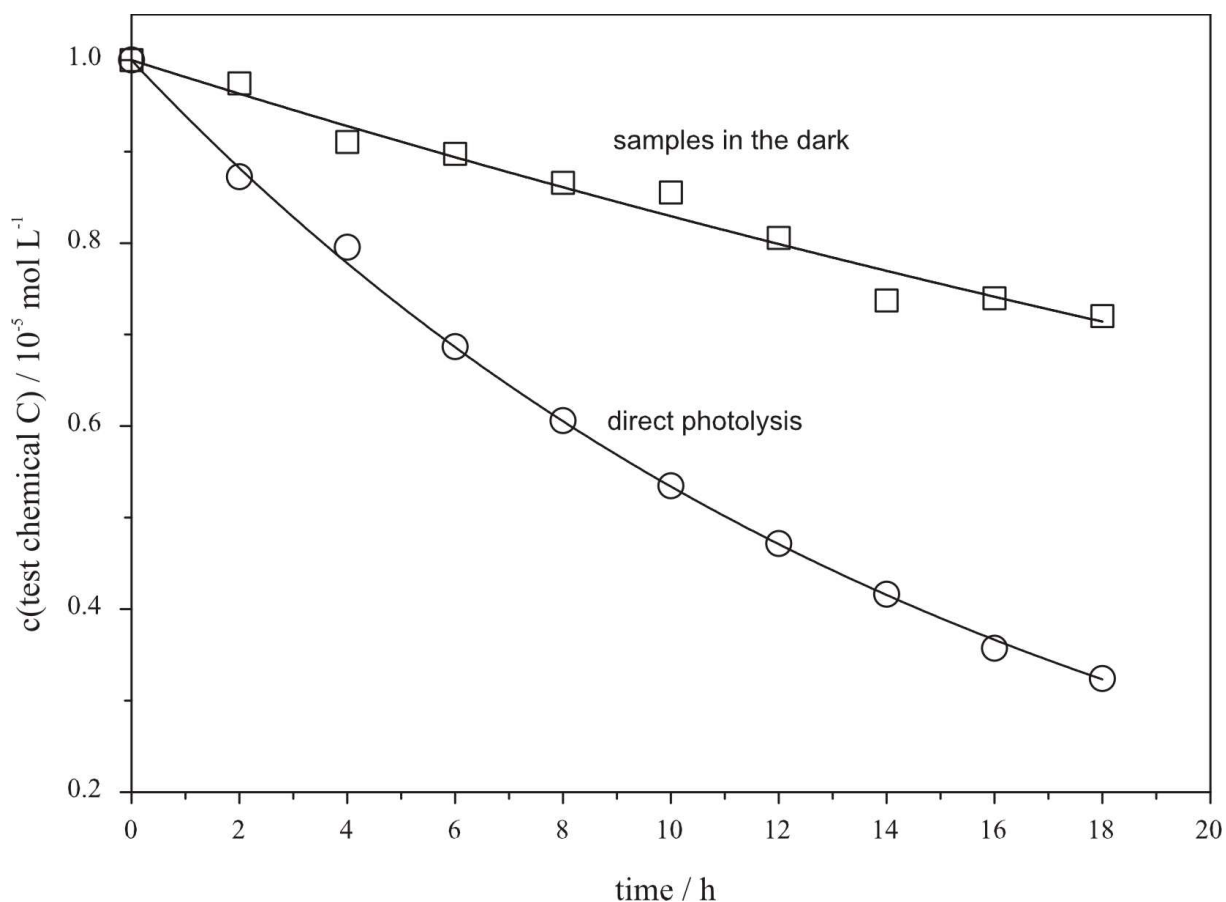


Figure 5: Experimental results obtained from direct photolysis (bullets) and in corresponding dark samples (squares) of test chemical C. Non-linear regression (lines) leads to $k_{\text{dark}} = 0.019 \text{ h}^{-1}$ and $k_{\text{irradiated}} = 0.063 \text{ h}^{-1}$, respectively.

A non-linear regression (see equation 2) leads to the rate constants for the dark control and photolysis experiment:

$$k_{\text{dark}} = 0.019 \text{ h}^{-1} \quad 7-1$$

$$k_{\text{irradiated}} = 0.063 \text{ h}^{-1} \quad 7-2$$

Using equation 11 the photolysis rate constant is:

$$k_{\text{d}} = k_{\text{irradiated}} - k_{\text{dark}} = 0.063 - 0.019 = 0.044 \text{ h}^{-1} \quad 7-3$$

The incident filtered xenon arc lamp photon irradiance $I_{0\lambda(\text{xenon})}$, obtained by actinometry, is necessary (an example of an actinometric measurement is shown below) to estimate the direct photolysis rate constant for the test chemical in near surface, clear natural water exposed to average daily solar photon irradiances L_{λ} (equation 12 in the body text):

$$k_{d(solar)} = \frac{1}{2.3} \cdot \frac{D_{cell}}{l} \frac{k_{d(xenon)} \sum_{290}^{800} \epsilon_{\lambda} L_{\lambda}}{\sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda(xenon)}} \quad 7-4$$

The corresponding data are summarized in Table 6 together with the molar decadic absorption coefficients of test chemical C (note the different molar decadic absorption coefficients in Table 4 and Table 6 due to the different wavelength intervals). Care has to be taken that the units of time are identical. Hence, in equation 12, $I_{0\lambda(xenon)}$ has the unit $\text{mmol cm}^{-2} \text{d}^{-1}$, $I_{0\lambda(xenon)}$ in Table 6 has the unit $\text{mmol cm}^{-2} \text{s}^{-1}$, k_d in equation 7-3 has the unit h^{-1} and $k_{d(xenon)}$ in equation 12 the unit d^{-1} . The unit conversion of $k_d = k_{d(xenon)}$ leads to:

$$k_d = k_{d(xenon)} = 0.044 \text{ h}^{-1} = 1.06 \text{ d}^{-1} \quad 7-5$$

The sum $2.3 \cdot \sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda(xenon)}$ is obtained by summing up the values in Table 6 (fourth column) with the necessary unit conversion, and leads to:

$$2.3 \cdot \sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda(xenon)} = 8.28 \cdot 10^{-5} \text{ s}^{-1} = 7.15 \text{ d}^{-1} \quad 7-6$$

To estimate the direct photolysis rate constant for test chemical C in near surface clear natural water at latitude 40° in summer the necessary sum $\sum_{290}^{800} \epsilon_{\lambda} L_{\lambda}$ was already obtained (see Table 5):

$$\sum_{290}^{800} \epsilon_{\lambda} L_{\lambda} = 0.545 \text{ d}^{-1} \quad 7-7$$

Using equation 12 (with $l = 1 \text{ cm}$ and the assumption $D_{cell} = 1 \text{ cm}$) the estimated direct photolysis rate constant for test chemical C in near surface clear natural water at latitude 40° in summer is:

$$k_{d(solar)} = \frac{D_{cell}}{2.3 \cdot 1} \frac{k_{d(xenon)} \sum_{290}^{800} \epsilon_{\lambda} L_{\lambda}}{\sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda(xenon)}} = \frac{1.06 \cdot 0.545}{7.15} = 0.081 \text{ d}^{-1} \quad 7-8$$

The half-life using $k_{d(solar)} = 0.081 \text{ d}^{-1}$ is $t_{1/2} = 8.6 \text{ d}$. Hence, as shown in Figure 1 and discussed in paragraph 17 and paragraphs 80-82, the half-life of 8.6 d is below the trigger value of 190 d and an identification of major transformation products is necessary and determination of the quantum yield is optional.

Table 6: Wavelengths (λ), molar decadic absorption coefficients ϵ_{λ} of test chemicals C, photon irradiances of the xenon lamp used ($I_{0\lambda(\text{xenon})}$) and the products $2.3 \cdot \epsilon_{\lambda} I_{0\lambda}$.

λ nm	ϵ_{λ} L mol ⁻¹ cm ⁻¹	$I_{0\lambda}$ mmol cm ⁻² s ⁻¹	$2.3 \cdot \epsilon_{\lambda} I_{0\lambda}$ s ⁻¹
290	1000	0	0
291	900	0	0
292	800	$1.56 \cdot 10^{-10}$	$2.87 \cdot 10^{-7}$
293	710	$7.74 \cdot 10^{-10}$	$1.26 \cdot 10^{-6}$
294	630	$1.53 \cdot 10^{-9}$	$2.22 \cdot 10^{-6}$
295	550	$2.48 \cdot 10^{-9}$	$3.14 \cdot 10^{-6}$
296	502	$3.62 \cdot 10^{-9}$	$4.18 \cdot 10^{-6}$
297	454	$4.73 \cdot 10^{-9}$	$4.94 \cdot 10^{-6}$
298	386	$6.20 \cdot 10^{-9}$	$5.50 \cdot 10^{-6}$
299	298	$9.17 \cdot 10^{-9}$	$6.29 \cdot 10^{-6}$
300	210	$1.22 \cdot 10^{-8}$	$5.89 \cdot 10^{-6}$
301	166	$1.55 \cdot 10^{-8}$	$5.92 \cdot 10^{-6}$
302	122	$1.98 \cdot 10^{-8}$	$5.56 \cdot 10^{-6}$
303	90	$2.41 \cdot 10^{-8}$	$4.99 \cdot 10^{-6}$
304	70	$2.87 \cdot 10^{-8}$	$4.62 \cdot 10^{-6}$
305	50	$3.36 \cdot 10^{-8}$	$3.86 \cdot 10^{-6}$
306	42	$4.12 \cdot 10^{-8}$	$3.98 \cdot 10^{-6}$
307	34	$4.60 \cdot 10^{-8}$	$3.60 \cdot 10^{-6}$
308	28	$5.30 \cdot 10^{-8}$	$3.41 \cdot 10^{-6}$
309	24	$6.30 \cdot 10^{-8}$	$3.48 \cdot 10^{-6}$
310	20	$7.34 \cdot 10^{-8}$	$3.38 \cdot 10^{-6}$
311	14	$8.59 \cdot 10^{-8}$	$2.77 \cdot 10^{-6}$
312	8	$1.00 \cdot 10^{-7}$	$1.84 \cdot 10^{-6}$
313	4	$1.19 \cdot 10^{-7}$	$1.09 \cdot 10^{-6}$
314	2	$1.36 \cdot 10^{-7}$	$6.26 \cdot 10^{-7}$
sum of column →			$8.28 \cdot 10^{-5}$

Determination of Quantum Yields (Optional)

Actinometry and Quantum Yield using a Monochromatic Light Source

The direct photolysis rate constant of $k_{d\lambda(\text{chem})} = 1.1 \cdot 10^{-3} \text{ s}^{-1}$ of a chemical E in aqueous solution was determined at $\lambda = 313 \text{ nm}$ on an optical bench in a quartz cuvette with $d_{\text{cell}} = 1 \text{ cm}$. Ten samples were irradiated and analyzed with a maximum irradiation time of 15 minutes. Concentrations were obtained by HPLC (with an uv-detector) and starting concentration of chemical E was $c_{0(\text{chem})} = 3 \cdot 10^{-6} \text{ mol L}^{-1}$. Dark samples show no degradation in the dark and concentrations were used without correction. The molar decadic absorption coefficient in water at $\lambda = 313 \text{ nm}$ was found to be $\epsilon_{\lambda(\text{chem})} = 5500 \text{ L mol}^{-1} \text{ cm}^{-1}$. Hence, the maximum decadic absorbance at 313 nm of chemical E was $A_{313(\text{chem})} = 0.0165$ ("optical thin" solution). A

corresponding actinometric measurement was performed with the same experimental setup using the iron oxalate actinometer (formation of Fe^{2+} from $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot 3\text{H}_2\text{O}$). Start concentration of the actinometer was $c_{0(\text{act})} = 0.15 \text{ mol L}^{-1}$ which leads to a decadic absorbance of $A_{313(\text{act})} \gg 2$. The concentration of Fe^{2+} formed for different irradiation times is shown in Figure 6.

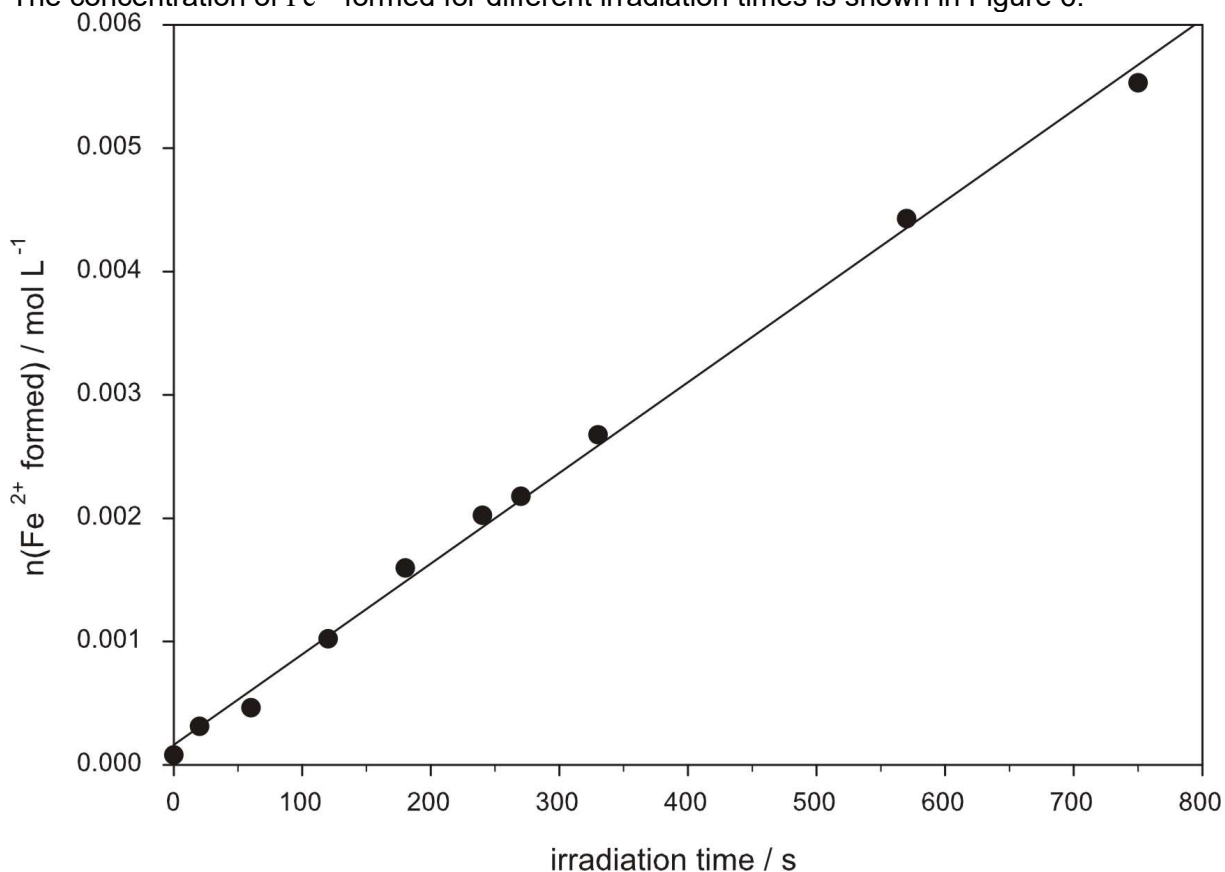


Figure 6: Formation of Fe^{2+} in an actinometric measurement using the iron oxalate actinometer ($c_{0(\text{act})} = 0.15 \text{ mol L}^{-1}$) at $\lambda = 313 \text{ nm}$. The slope of the line leads to $k_{d\lambda(\text{act})(\text{zero order})} = 7.35 \cdot 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$.

The slope of the line in Figure 6 leads to $k_{d\lambda(\text{act})(\text{zero order})} = 7.35 \cdot 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$. Using equation 17 (paragraph 97) the quantum yield of chemical B at $\lambda = 313 \text{ nm}$ is therefore:

$$\Phi_{chem,313 \text{ nm}} = \frac{\Phi_{act}}{2.3 \epsilon_{\lambda(\text{chem})} D_{cell}} \frac{k_{d\lambda(\text{chem})}}{k_{d\lambda(\text{act})(\text{zero order})}} = \frac{1.24}{2.3 \cdot 5500 \cdot 1} \frac{1.1 \cdot 10^{-3}}{7.35 \cdot 10^{-6}} = 0.015 \quad 7-9$$

Quantum Yield using a Polychromatic Light Source

If the photon irradiance of a xenon light source is known at all wavelengths, as already discussed in the example for test chemical C, equation 5 can be used to calculate the quantum yield of a test chemical. Hence, rearranging equation 5 leads to:

$$\Phi = \frac{D_{\text{sys}}}{2.3 \cdot 1} \cdot \frac{k_d}{\sum_{290}^{800} \epsilon_{\lambda} \cdot I_{0\lambda}} \quad 7-10$$

The mean quantum yield of test chemical C in the wavelength interval $\Delta\lambda = 292 - 314 \text{ nm}$ can be

obtained using the values $l = D_{\text{sys}} = 1 \text{ cm}$, $k_d(\text{xenon, test chemical C}) = 0.044 \text{ h}^{-1} = 1.22 \cdot 10^{-5} \text{ s}^{-1}$ and

$$2.3 \cdot \sum_{290}^{800} \epsilon_{\lambda} I_{0\lambda(\text{xenon})} = 7.15 \text{ d}^{-1} = 8.28 \cdot 10^{-5} \text{ s}^{-1} \quad 7-11$$

Using equation 7-10 the quantum yield of test chemical C is therefore:

$$\Phi = \frac{1.22 \cdot 10^{-5}}{8.28 \cdot 10^{-5}} = 0.15 \quad 7-12$$