

2.5 *Test Methods for Abiotic Degradability*

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2.5.1 INTRODUCTION

Organic chemicals which enter the environment following their use can be degraded or transformed in several different ways. The resulting decomposition or transformation process will depend, among other factors, on the environmental compartment into which the chemicals are released and transported. Organic compounds in aquatic systems and soils are primarily decomposed biologically, while those substances which enter the atmosphere are predominantly degraded or transformed photochemically, therefore only photochemical processes are considered in this section.

A photochemical process can ensue by either direct or indirect activation (primary or secondary degradation) of the organic molecule. In the first case, the organic molecule absorbs light within the region of the solar spectrum (290–450 nm) and reacts without further collaboration of another species. In

terms of quantitative transformation, direct photolysis is of minor importance because a number of environmentally relevant organic substances do not absorb radiation within the 290–450 nm range. By contrast, the degradative processes which proceed under the influence of reactive species (secondary degradation) are of greater significance in terms of both the variety of organic compounds affected and the total rate of transformation.

The photoreactivity of organic chemicals in aquatic systems has been investigated by a number of authors (e.g. Zepp and Cline, 1977; Mill *et al.*, 1980a and see discussion in Chapter 3.1) and, in conjunction with biological decomposition processes and hydrolysis, is vital to the degradation of chemicals in water bodies and the adsorbed phase. In important measure, photochemically induced degradation of chemicals in aqueous systems and natural waters is governed by the concentrations of humic substances, suspended sediments and salts. However, the quantitative influence of these constituents on photochemical degradation rates has not yet been fully assessed. To a large extent photoreactions of chemicals adsorbed on soils have been only superficially investigated.

2.5.2 CRITERIA FOR ESTABLISHING TEST METHODS

The mechanisms of photodegradation of organic compounds in nature (in the atmosphere and in waters) are extremely complex. Existing information on the atmospheric breakdown of organic substances originates almost exclusively from laboratory experiments (smog chamber experiments). Such smog chamber experiments are an attempt to simulate atmospheric conditions in the laboratory. However, such simulations are extremely problematic and involve considerable experimental outlay. Most test methods have therefore attempted to simulate only the most important boundary conditions essential for the abiotic decomposition of organic chemicals in the environment. These include the proper nature of the microcompartment, concentration and types of test and reactive species, and the spectral distribution of the light source.

In addition to reproducibility and standardization, photochemical degradation test methods should fulfil these further requirements:

- (a) A precise characterization of the light source; if natural light is not used,
- (b) Suitable and sensitive analytical methods identifying and quantifying the substance and the reaction products,
- (c) Ecological relevance (see Section 2.5.4),
- (d) Automation, if possible.

2.5.3 TEST METHODS

Currently, there are three generally accepted proposals for the comparative testing of photodegradation. These methods are the GSF test, the EPA test

and the Fujiki test. These test procedures are well documented and have been employed by a large number of research groups. This evaluation is focused only on these accepted testing techniques and does not treat specific research methodologies for the mechanistic and reaction rate analysis of atmospheric contaminants.

2.5.3.1 The GSF test (Kotzias *et al.*, 1979; Lotz *et al.*, 1979; OECD, 1979a)

The GSF test is based on the photochemical breakdown of organic chemicals adsorbed on silica gel through the action of solar UV radiation (Gäb *et al.*, 1977; Schmitzer *et al.*, 1980). In the GSF photomineralization test, the total decomposition of organic compounds is measured only in terms of the CO₂ formed.

Irradiations are carried out in a double-walled, cylindrical borosilicate or quartz reactor with an additional cooling jacket. A mercury high-pressure lamp adjusted to begin emitting at 290 nm, through the insertion of borosilicate glass filters, serves as the light source. The light is located in the centre of the cylindrical apparatus. Standardized silica gel with surface

Table 2.5.1 Photomineralization results for selected organic chemicals using the GSF method

Chemical	Applied concentration (ng/g silica gel)	Photo-mineralization (%)	Organic fragments (%)
2,4,6-Trichlorophenol	78	65.8	0.1
Pentachlorophenol	82	62.0	0.1
Aniline	39	46.5	0.8
Hexachlorocyclopentadiene	64	46.0	0.1
Benzidine	125	40.8	0.1
<i>p</i> -Nitrophenol	83	39.1	0.2
Trichloroethylene	7983	36.8	1.3
Naphthaline	183	30.0	0.1
Benzene	32	15.2	0.6
Benzoic acid	200	10.2	0.1
Biphenyl	76	9.6	0.1
Aldrin	45	8.8	0.1
Nitrobenzene	60	6.7	0.1
γ -Hexachlorocyclohexane (Lindane)	33	6.4	0.1
<i>p</i> -Chlorobenzoic acid	30	6.3	0.1
DDT	83	5.4	0.1
2,2'-Dichlorobiphenyl	77	3.5	0.1
<i>n</i> -Dodecane	243	2.9	0.7
2,4-Dichlorobenzoic acid	30	2.8	0.1
Carbon tetrachloride	374	1.0	3.5

adsorbed organic compound is placed in the reactor and irradiated for a specific time. The liberated carbon dioxide is measured with an infrared CO₂ analyser. Both solids and liquids lend themselves well to this method while volatile compounds and gases can also be investigated using appropriate modifications. The sensitivity of the method is determined by the CO₂ analyser. The GSF test system accommodates the use of ¹⁴C-labelled substances, therefore enabling irradiations to be performed in the p.p.b. range (see Table 2.5.1)

2.5.3.2 The EPA test (EPA, 1979)

In the EPA test, organic chemicals dissolved in water are exposed to solar radiation. No complex test apparatus is required although Pyrex flasks must be used. The disappearance of the test substance is measured and its half-life calculated according to the procedure proposed by Zepp and Cline (1977). They demonstrated that the rate constant for the disappearance of an organic compound dissolved in water can be calculated by using the formula

$$\log \frac{C_0}{C} = \frac{K_p t}{2.30}$$

where C is the concentration at time t , C_0 is the starting concentration and K_p is the rate constant.

The half-life is given by the formula

$$t_{1/2} = \frac{0.693}{K_p}$$

In the EPA test, decomposition and disappearance of the starting substance are followed by gas chromatography, UV or other analytical techniques. The

Table 2.5.2 Photochemical degradation in water phase using the EPA test; data from Hustert *et al.* (1981)

Chemical	Solubility (H ₂ O)	Concentration	Photodegradation	
			K_p (days ⁻¹)	$t_{1/2}$ (days)
C ₆ H ₆ (HCB)	5 g/l	1	0	
CCl ₄	77 mg/100 ml (20°)	1	0	
CH ₃ OH		3	0	
C ₆ H ₆	181 mg/100 ml (20°)	1	0.041	16.9
<i>p</i> -NO ₂ -C ₆ H ₄ OH	1.18 g/100 ml (25°)	2	0.121	5.7 (pH 5)
			0.103	6.7 (pH 7)
			0.0505	13.7 (pH 9)

Concentration: 1 = half the solubility in H₂O, 2 = 10⁻⁵ molar, 3 = 50 mg/100 ml (20°).

sensitivity of the EPA system depends on the sensitivity of the analytical method used to determine the residual concentration of the specific test compound. The lower limit of quantification can be depressed significantly with the use of radio labelled compounds. The EPA method is applicable to all chemicals which both absorb light above 290 nm and are sufficiently water-soluble to be analysed in solution (see Table 2.5.2). Further discussion of the EPA test can be found in Chapter 3.1.

2.5.3.3 The Fujiki test (OECD, 1979b)

In the Fujiki test system, the organic chemical being investigated is irradiated inside a quartz reaction flask (of approx. 3 l volume) with UV light ($\lambda = 300$ nm and 360 nm). The degree of photodegradation is defined as the difference between the initial and final concentrations. As final concentrations are measured by gas chromatography, the sensitivity of this technique determines the sensitivity of the Fujiki method.

This method can be used for gaseous chemicals and for those compounds which can be converted into the gases. Selected examples of photochemical degradations of volatile compounds are presented in Table 2.5.3.

Table 2.5.3 Photochemical degradation of gaseous organic compounds using the Fujiki test

Chemical	Photodegradation after	
	6 h (%)	24 h (%)
Benzene	48.9	61.6
1,2,4-Trichlorobenzene	6.7	75.5
Carbon tetrachloride	40.0	43.3
Methanol	31.0	46.8
Aniline	60.0	84.9

2.5.4 EVALUATION OF THE TEST METHODS: DISCUSSION OF THE ENVIRONMENTAL RELEVANCE

The methods briefly described, the GSF, EPA and Fujiki tests, have been the subject of lengthy critical discussions at both the national and international level (Funke *et al.*, 1980). It is the ecological relevance of these simple test methods which is the primary topic of debate. Attempts have been made to correlate the data obtained from these tests with data from experiments conducted under less artificial environmental conditions such as smog chamber studies. Such comparisons, however, have been limited, as current

techniques for simulating atmospheric (tropospheric) conditions in the laboratory are still rather unrefined. Nevertheless, it would be inconsistent to only consider these comparative test methods in isolation. Results from these tests must be, whenever possible, integrated into a larger testing framework, from which accurate quantitative predictions of photochemical degradation in the natural environment can be made.

The structure of the ecosphere is so complex that a sharp separation and comprehensive characterization of the individual environmental compartments, for example, a pure gas phase or a pure aqueous phase, is impossible even in the more complex simulation experiments. It is therefore more effective to establish the test method on the basis of selected ecologically relevant parameters, which have been demonstrated to govern the reactions or behaviour of a chemical in the environment, than it is to quantify individual 'phase' processes.

The assigning of individual test methods to the different environmental compartments (e.g. water method, gas-phase method, etc.) has therefore been deliberately avoided. Instead, these methods are evaluated with respect to their contribution to understanding the whole process of photodegradation.

The described methods presently take into account ecologically relevant parameters such as the intensity and spectral distribution of the irradiation source, the moisture, the pH, and the micro-environment where the test substance is likely to occur (the state of the compound after use and distribution in the ecosphere, i.e. adsorbed on surfaces, as dust particles, dissolved in water, etc.).

The GSF method has been applied to a number of chemicals and it serves primarily as a means of establishing priority (ranking) lists leading to further ecochemical investigations. The environmental relevance of a GSF test result is, among other things, determined by the validity of quantitative estimates of mineralization products (CO_2 , HCl, Cl_2 , etc.) as correlated with the monitored fate of the test substance in the atmosphere.

The UV spectra of molecules adsorbed (on silica gel) differ appreciably from those in solution or in the gas phase. In most molecules such an adsorption on silica gel (a polar carrier) leads to a hypsochromic or bathochromic shift of the absorption bands. A displacement towards smaller wavelengths (hypsochromic) is observed during $n-\pi^*$ transitions, while a shift in the opposite direction (bathochromic) occurs with $\pi-\pi^*$ transitions in aromatic systems. Organic molecules, in the dissolved or gaseous state, which do not absorb in the solar spectral region, can thus be activated and transformed in the adsorbed form by UV irradiation.

In addition to direct photolysis, reactions with reactive species on surfaces may be important in terms of photomineralization. One indication of this could be a differential photoreactivity in air and in pure oxygen (Kotzias *et al.*,

1981). Since the atmosphere contains particles with detectable residence times, photoreactions of organic molecules in the adsorbed phase are relevant to the photochemical behaviour of organic impurities on the earth's surface and for particle-bound portions of organic chemicals in the atmosphere. Biodegradation and hydrolysis are the most important pathways for eliminating organic chemicals in aquatic systems; photodegradation is significant for those organic substances which can undergo only partial or no biological or hydrolytic transformation.

Photodegradation in aqueous systems can ensue both via direct photolysis and also, as recent studies have shown, via secondary reactions with highly reactive radicals such as $\text{RO}_2\cdot$, $\cdot\text{OH}$, etc. (Mill *et al.*, 1980 a and b). In the EPA test, chemical breakdown photolysis at varying pH values is followed analytically. Thus, the EPA test contributes to the understanding of the behaviour of organic chemicals in the ecosphere by comparing tests of photochemical transformations under conditions of natural light, with tests of the chemicals degradation in water.

In the modified Fujiki test (Mansour *et al.*, 1981), some problems present in the original version have been eliminated, thus allowing comparative testing of photochemical degradation of gases and substances of high vapor pressure. Wall reactions almost certainly play a large role in this test and need to be allowed for in the evaluation of results. The Fujiki test is very suitable for comparative studies of the breakdown of gaseous organic compounds and is relatively economical after the initial purchase of necessary apparatus.

2.5.5 PROCEDURAL WORK RELATING TO THE DEVELOPMENT OF METHODS TO ASSESS THE FATE OF ORGANIC CHEMICALS IN THE ATMOSPHERE

A number of procedural studies have dealt with assessing the behaviour of synthetic organic chemicals in the atmosphere. The proposal of Hendry (Mill *et al.*, 1980b) and Klöpffer (1980) and the ASTM (1979) 'proposed standard' merit specific mention. These procedures should be regarded as test methods for evaluating photochemical degradation in the 'gas phase'.

The method proposed by Hendry and the ASTM 'proposed standard' are based on the determination of OH and O_3 reactivities and on the characterization of photoproducts (ASTM method). The reactions of the OH radicals and O_3 with organic chemicals take place in a 100-litre Teflon bag. The OH radicals are generated by HONO photolysis (Mill *et al.*, 1980b).

Klöpffer (1980) proposed a test procedure in which chemical-OH radical reactions in solution simulate comparable degradation processes in the 'gas phase'. Reactions of OH radicals with organic compounds in solution are easier to control than those in the gas phase if a suitable source of the OH radicals is available. Klöpffer suggests the use of Fenton's reagent

($\text{H}_2\text{O}_2 + \text{Fe}^{2+}$) to generate the OH radicals in solution. These radicals then react directly with the chemical under investigation. Degradation rates would be comparable to those of other compounds tested in this system.

2.5.6 CONCLUSION

The objections raised as to the environmental relevance of simple and inexpensive test methods are understandable. However, one must remember that to date all results of basic environmental chemical testing (base-set water solubility, distribution coefficient, hydrolysis, etc.) and all data obtained from more elaborate test systems, including smog chamber studies, can be only qualitatively and not quantitatively extrapolated to the natural environment. The ecosphere is such a complex system that it cannot be reproduced with any degree of precision in the laboratory. Each and every simulation is necessarily accompanied by errors, and therefore an ecotoxicological assessment of organic chemicals behaviour is semiquantitative at best and prediction of fate in the natural system calls for judgemental decisions. At this stage, however, the short-term tests provide much of the data essential for initial screening programs for the purpose of ranking compounds as a basis for further testing. Gathering the same results with classical techniques would entail an enormous investigative expenditure.

If necessary, the initial assessment of photochemical degradation and transformation should be supplemented with more detailed advanced studies. These experiments should identify specific reactions which enhance the predictability of short-term test results.

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