3.1

Abiotic Chemical Changes in Water

H. HULPKE and R. WILMES
BAYER A.G., Forschungszentrum
Postfach 130 105
D-5600 Wuppertal
Federal Republic of Germany

3.1.1 Introduction .................................................. 119
3.1.2 Transport Mechanisms ........................................ 121
  3.1.2.1 Volatilization from water ............................... 121
  3.1.2.2 Adsorption and bioaccumulation ....................... 122
3.1.3 Abiotic Degradation Pathways in Aquatic Systems ... 122
  3.1.3.1 Hydrolysis ............................................. 122
  3.1.3.2 Photodegradation ...................................... 125
  3.1.3.3 Sensitized photodegradation ......................... 127
  3.1.3.4 Indirect photodegradation and oxidation .......... 128
  3.1.3.5 Anthropogenically induced transformations of organic compounds in water .............. 129
3.1.4 Possibilities for a Comprehensive Estimation of Mobility and Degradation in Water .................. 130
  3.1.4.1 Model ecosystems .................................. 130
  3.1.4.2 Estimation of environmental behaviour from laboratory data and properties of the substance 131
3.1.5 Summary and Conclusions .................................. 132
3.1.6 References .................................................... 133

3.1.1 INTRODUCTION

Approximately 71% of the earth's surface is covered by water. Of the $1.380\times10^{12}\text{ m}^3$ water on the earth, however, a mere $230\times10^{12}\text{ m}^3$ is freshwater in lakes and rivers. Another $7000\times10^{12}\text{ m}^3$ is ground water and $13\times10^{12}\text{ m}^3$ is in the atmosphere according to Global 2000 (1980). The freshwater reserves are intensively used by man. Rivers, lakes and to some extent ground water are thus exposed to great pollutant burdens from anthropogenic sources. This problem is exemplified by the introduction of huge quantities of inorganic salts and organic chemicals into rivers, lakes, and the oceans via waste effluents, soil leaching and from dry fallout and precipitation from the atmosphere.
Compared with the other major environmental compartments (soil and air), water occupies an intermediate position in terms of its heterogeneity, variability and mobility. Substances dissolved in water can be transported over vast distances by passive distribution or active transport in currents. At the same time these compounds are exposed to numerous physical, chemical and biochemical processes which can transform and then degrade them or transfer them into the biota, sediments or atmosphere.

Aquatic systems are composed of water, sediment and living or dead organic material. These components are intimately related to one another as indicated by the following simple scheme:

![Diagram of aquatic system components]

The composition of the above-named components, their condition and relative proportions can vary within wide limits.

Properties and conditions of aquatic systems, which influence the mobility and degradation of the organic substances, can be listed as follows (Johnson et al., 1978):

1. Surface area.
2. Depth.
3. pH.
4. Flow rate and composition of the sediment.
5. Salt content.
6. Concentration of suspended sediment.
7. Nutrient content.
8. Light absorption properties.

Naturally occurring chemicals leached from the soil system also have a major influence on transport and degradation processes occurring in water. These chemicals are mainly salts and humic compounds. The latter are mostly derived from decay of the vegetation. Humic substances are polymeric with molecular weights from several hundred to many million daltons. They are composed of phenols, benzoic acids, fatty acids and alcohols joined together in a cross-linked polymeric system. Humic compounds are divided into three fractions according to their solubility (Khan, 1980):
(1) Fulvic acids.
(2) Humic acids.
(3) Insoluble humic material.

As soluble compounds with relatively low molecular weights, fulvic acids, in particular, influence the transport and degradation of chemicals in water. Their ability to form complexes with metal ions plays a role. Humic compounds are also thought to be involved in the formation of singlet oxygen and perox radicals.

### 3.1.2 TRANSPORT MECHANISMS

There are three basic transport mechanisms by which a substance dissolved in water can be eliminated from the water without undergoing a chemical change:

1. Volatilization from the water.
2. Adsorption on the sediment.

These routes of physical translocation are dealt with in detail in Chapters 3.2, 4.4, and 5.

#### 3.1.2.1 Volatilization from Water

Hydrophobic, water insoluble compounds often have a high tendency to volatilize from aqueous solutions even when they have low vapour pressures. The volatility of such compounds is particularly difficult to experimentally determine in a reproducible fashion from which results can be reliably extrapolated to conditions in the environment. A number of experimental procedures have been described (Dilling, 1977; Yang and Wang, 1977; Kilzer et al., 1979; Smith and Bomberger, 1980).

In addition, attempts have been made to estimate volatilization from water mathematically on the basis of physico-chemical parameters. One scientifically accepted model which is frequently used is based on two interfacial layers which influence the exchange of a chemical between the two compartments air and water (Liss and Slater, 1974). Transport processes within these boundary layers can be described by phase transition coefficients which themselves depend on the diffusion coefficients of the chemical in the corresponding medium (Wolff and van der Heijde, 1982).

For substances with low vapor pressure, volatility from water is difficult to determine experimentally. However, it is possible to estimate volatile loss from the value of the Henry constant (H) if volatilization from water is expected.
The Henry constant is the ratio of the saturation vapor pressure and water solubility of a substance. It is given, for example, in the units atm ⋅ m³ ⋅ mol⁻¹. When the Henry constant is large (H > 10⁻³ atm ⋅ m³ ⋅ mol⁻¹) only the phase transition resistance on the water side hinders the substance from evaporating. For smaller Henry constant values (H < 10⁻⁵ atm ⋅ m³ ⋅ mol⁻¹) the phase transition resistance on the gas side is more important and the substance stays mainly in solution (Mackay, 1978) (see Chapter 5 for additional details).

3.1.2.2 Adsorption and Bioaccumulation

Adsorption or bioaccumulation must be taken into account particularly in the case of highly hydrophobic, relatively water-insoluble compounds.

Unique adsorption behaviour is to be expected with ions and ionizable substances. Such substances can be shielded effectively for long periods from further degradation reactions and transport mechanisms by adsorption on sediment. On the other hand, the reactivity and UV absorption properties of substances can change when they are adsorbed on sediment. Furthermore, various other types of reactions are facilitated by such changes in micro-environments.

3.1.3 ABIOTIC DEGRADATION PATHWAYS IN AQUATIC SYSTEMS

The abiotic degradation of organic chemicals in water can be classified as follows:

(1) hydrolysis.
(2) light-induced degradation.
(3) miscellaneous degradation reactions.

3.1.3.1 Hydrolysis

General features

The term hydrolysis describes those reactions of organic chemicals which involve cleavage of the molecule by water.

\[ RX + H_2O \rightarrow ROH + HX \]

In many cases water is not itself the reactive species. Attack and cleavage of the molecule is initiated by OH⁻ or H₂O⁺ ions. The hydrolysis process can thus be divided into reactions catalysed specifically by H₂O⁺ or OH⁻ ions and the neutral reaction with H₂O. In addition other types of reaction, \( k_c [\text{catalysts}] \cdot RX \), must be considered. These include catalytic phenomena such as the influence of basic anions and the effects of other salts (Mabey and Mill,
1978). The hydrolysis process can then be represented as:

\[
\frac{-d[RX]}{dt} = k_{Hy} \cdot [RX]
\]

\[
= k_A \cdot [H_3O^+] \cdot [RX] + k_B \cdot [OH^-] \cdot [RX] + k_N \cdot [H_2O] \cdot [RX] + k_c \cdot [catalysts] \cdot [RX]
\]

At constant temperature and pH, the hydrolysis occurs as a pseudo-first order reaction and the half-life is independent of substrate concentration.

\[ t_{1/2} = \frac{0.693}{k_{Hy}} \]

The temperature dependence of the hydrolysis constant \( k_{Hy} \) may be obtained from the Arrhenius equation

\[ k_{Hy} = k_m \cdot e^{-E_A/RT} \]

when converted to the logarithmic form, \( \ln k_{Hy} = \ln k_m - E_A/RT \), where \( k_m \) is the maximum hydrolysis constant and \( E_A \) is the activation energy.

Graphically the temperature dependence of the hydrolysis reaction may be presented in the form of a straight line by plotting \( \log k_{Hy} \) against \( 1/T \). The hydrolysis constant at any given temperature can thus be obtained by the extrapolation of data already available.

**Laboratory Experiments**

Laboratory experiments on hydrolysis are normally carried out in buffer solutions in order to maintain a constant pH. However, the relatively high concentration of ions necessary for the buffering can cause salt-effects which can accelerate or decelerate the rate of hydrolysis. These effects stem from (1) changes in the activity coefficients for strongly polar or ionic test substances, (2) influences on a polar transition state in the hydrolysis reaction, or (3) catalytic actions or reactions of nucleophilic anions such as HPO$_4^{2-}$, Cl$^-$ or Br$^-$ (Mabey and Mill, 1978).

Although the use of buffers is a simple and experimentally reproducible method for maintaining a constant pH value in laboratory experiments, salt-effects due to the use of buffers in a hydrolysis experiment can be avoided by controlling the pH value with a pH-stat titrator at defined ionic strength.

Due to the low concentrations of H$^+$ and OH$^-$ in natural waters within the pH range (5–9) common in the environment, the importance of acid- or base catalysed reactions can be relatively small, therefore, the above-mentioned salt-effects can make a substantial contribution to hydrolysis in strongly buffered laboratory solutions and possibly in freshwater aquatic systems. In natural freshwater systems ionic strengths are relatively low (up to 1 g·m$^{-3}$), but in seawater (salt content about 3.5%) they are high. The oceans are
buffered systems with a pH value of about 8.3 and contain a multitude of different anions and cations (see Korte, 1980).

Other catalytic effects can be caused by metal ions (Ketelaar et al., 1956). However, Mabey and Mill (1978) have expressed the opinion that, owing to the very low concentrations of catalytically active substances, these should be of little significance to chemical degradation in the aquatic environment, particularly as they are often present in complexed forms.

Substances can be shielded from hydrolytic attack by adsorption on sediment. Most investigations of adsorbed organic compounds on sediments, though, have been concerned with photodegradation (e.g. Miller and Zepp, 1979a and b; Zepp and Schlotzhauer, 1981). Results from experiments with clays as catalysts in hydrolysis reactions (Mingelgrin et al., 1979) suggest that such effects are also possible with sediment adsorbed chemicals. The influence of humic substances upon the hydrolysis of certain compounds has also been reported (e.g. Khan, 1978).

To establish the hydrolytic behaviour of test substances, preliminary tests are usually carried out by first estimating hydrolytic stability and then, where necessary, more detailed investigations are undertaken to determine the half-life of the compound under environmental pH and temperature conditions. The preliminary tests can be carried out by measuring the rate of hydrolysis at higher temperatures (OECD, 1981) or at relatively high concentrations of OH⁻ or H⁺ ions (Mill et al., 1980a). When the estimated half-life is greater than 1 year, further studies are often not necessary.

Auxiliary solvents are frequently used in hydrolysis experiments with highly hydrophobic compounds to facilitate studies within concentration ranges which are easier to analyse. Alcohols, dioxane, acetone and other water-miscible solvents can be used as co-solvents. However, the use of co-solvents should be avoided, in as far as possible, because they can have a marked influence on the rate of hydrolysis and make the pH of such a mixture difficult to determine (Mabey and Mill, 1978). It is therefore recommended that co-solvents be used only when absolutely necessary, and when used, only at a concentration of 0.05% to 1% (e.g. OECD, 1981). However, the environmental relevance of data from experiments using these relatively nonpolar co-solvents (unpolar, that is, compared to water) may be acceptable. Most highly hydrophobic organic compounds in natural waters tend to concentrate in relatively nonpolar surroundings such as surface films, suspended organic matter, etc. as they would associate with co-solvents in experimental solutions (Södergren, 1978).

It is obvious from the above description that test methods designed to probe the hydrolytic behaviour of organic substances certainly do not cover the entire spectra of phenomena possible in the environment. None the less, these techniques are of great value in that the quasi ‘inherent hydrolysability’
of compounds can be determined under standardized conditions and thus, the results among various substances are comparable.

Even if a substance exhibited a total lack of degradability in the hydrolysis tests described, it can still be broken down due to catalytic effects in the environment. Laboratory tests in such cases must be considered inadequate for the prediction of degradation in the environment. In cases where such special mechanisms could be operating, simulating experiments with natural waters should be undertaken to confirm the extrapolation of laboratory findings to environmental conditions.

### 3.1.3.2 Photodegradation

**General features**

Direct or primary photodegradation refers to those degradation reactions of organic substances in an excited electronic state following the absorption of light energy by the compound being degraded. Numerous reactions are possible, ranging from simple isomerization of the molecule to cleavage or chemical changes in substituents, or to complete mineralization.

Direct photodegradation can only occur in the environment when the substance is able to absorb available light. Due to the protective ozone layer in the stratosphere, only light of wavelengths longer than 285–290 nm generally reaches the earth’s surface. Shortwave radiation around 300 nm is of particular interest as its energy is sufficient to cleave a whole series of organic bonds \( E_{300\text{nm}} = 398 \cdot 10^3 \text{ joule mol}^{-1} \). The intensity of this shortwave radiation around 300 nm is very low in the environment. In addition, intensity also depends upon latitude, time of day, season and climatic variations (see Johnson et al., 1976).

The UV absorption spectrum of a substance in water is thus an important piece of basic information concerning its direct photodegradation. The spectrum demonstrates whether degradation is possible under environmental conditions. However, the UV absorption of an organic substance is highly dependent on its immediate surroundings. Either bathochromic or hypsochromic UV absorption shifts can occur when a substance is, for example, adsorbed on suspended sediment or dissolved in a surface film.

As many organic chemicals have only very slight UV absorption in the area of 300 nm, it is often difficult to assess from UV spectrum data whether, in fact, photodegradation in the environment can occur. It is possible in these cases that the observed UV absorption could stem from a strongly absorbing impurity.

The degradability of a compound electronically excited by light energy can be characterized by the quantum yield of the degradation (see discussion in
Chapter 2.4). Quantum yield is defined as the number of degraded molecules per number of light quanta absorbed.

\[ \Phi = \frac{R}{\int_{\lambda_1}^{\lambda_2} I_a(\lambda) \, d\lambda} \text{ (mol} \cdot \text{einstein}^{-1}) \]

where \( R \) = rate of disappearance (mol \cdot l^{-1} \cdot s^{-1})

\( I_a \) = absorbed light intensity (einstein \cdot l^{-1} \cdot s^{-1})

\( \lambda_1, \lambda_2 \) = spectral range (overlap of the incident light and the absorption of the compound).

Quantum yields can vary widely. Values range from much greater than 1 (chain reactions) to slightly over 1 (primary dissociations), down to far smaller than unity.

In experiments involving low substrate concentrations, the reaction partners (light, water and oxygen) are present in excess and thus the degradation reactions observed usually follow pseudo-first order kinetics. Similar circumstances are expected in the environment.

‘Environmentally relevant’ half-lives can be calculated from the quantum yield of the degradation, the UV absorption spectrum in aqueous solution and sunlight emission values at the earth’s surface. Depending on the extent of the available data it may be possible also to account for latitude, water depth and diurnal variation in sunlight intensity (Zepp and Cline, 1977).

In natural waters, direct photodegradation can be influenced in many different ways. Two fundamental factors can be differentiated:

(1) Effects on the possibility of interaction between light and substrate.

(2) A change in the reactivity of the substrate.

The first mechanism includes adsorption, bioaccumulation, and other phenomena which shield the chemical from light radiation. Other substances in the water (humic acids) compete with organic compounds for the limited quantity of available solar radiation. Also, the degree of ionization, complex formation and change due to adsorption phenomena will affect both UV absorption and the reactivity of organic compounds (e.g. Miller and Zepp, 1979a and b; Zepp and Schlotzhauer, 1981).

As a first approximation, the primary process of a photodegradation (e.g. dissociation following absorption of light) can be assumed to be independent of temperature. However, the subsequent reactions which compete with recombination can themselves be temperature dependent. Therefore, the temperature in photolysis experiments should correspond to that expected in the particular environment.

\textit{Laboratory experiments}

Tests on photodegradation in water are carried out either with sunlight (e.g.
the EPA test; Leifer and Stern, 1978) or artificial light sources. Sunlight can be regarded as the 'most environmentally relevant' light source. However, differences in the intensity of sunlight during various studies make the comparison of experimental results difficult. In the spectral range relevant to degradation, differences and variations in sunlight intensity in the wavelength range up to 400 nm can be compensated for with special actinometers (Mill and Hendry, 1980) or by simultaneous irradiation of reference substances. The possible discrepancies due to long experimental times when using sunlight as compared to shorter irradiation in laboratory experiments using artificial light sources of higher intensity must also be considered.

When artificial light sources are used, there is, on the one hand, the possibility of determining quantum yields for compounds irradiated with monochromatic light and then calculating 'environmental half-lives' as described previously. This procedure assumes that the value of the quantum yield is only slightly dependent upon the wavelength of the radiation. This assumption can be regarded as valid when excitation levels in the same electronic transition state are being considered. When polychromatic light is used there are potential difficulties with a reliable cut-off at lower wavelengths. This problem is particularly relevant to the large number of compounds having only a slight light absorption at around 300 nm. Large differences in the stability of such compounds are found, depending on the thickness and composition of the borosilicate glass normally used as a filter. One way of solving this problem is the irradiation of reference substances with similar UV absorption properties using conditions similar to those used for the test compound.

Photodegradation tests should only be carried out in buffered solutions when, due to certain intrinsic properties (e.g. ionizability), photodegradation behaviour is expected to be dependent upon pH. In all other cases buffering merely creates an additional artificial condition. Experiments in double-distilled water are usually a measure of the maximum photostability of a compound as tests in 'natural' water normally produce shorter half-lives.

Therefore, laboratory photodegradation experiments in water provide only a measure of the intrinsic photodegradability of a compound under standardized conditions. Even though experimental conditions should be as close as possible to those in the environment, a wide spectrum of possible influences on direct photodegradation in natural aquatic systems cannot be simulated.

3.1.3.3 Sensitized Photodegradation

The term sensitization is applied when light energy is not taken up directly by the substance but is transferred from an excited donor to the compound being degraded.
Substances which upon absorption of light energy can cross from the singlet to the triplet excited state, are potential sensitizers. Due to the relatively long lifetime of the triplet state, their energy can be transferred to an acceptor molecule. The acceptor itself is then in an excited state and can often react rapidly in manifold fashion due to the long lifetime of this excitation.

Potential sensitizers in the environment are humic acids, fulvic acids, flavonoids and diverse other natural products. Triplet energies of naturally occurring sensitizers are often very low (e.g. chlorophyll A: $E_{\text{Triplet}} = 158 \cdot 10^3$ joule $\cdot$ mol$^{-1}$). Model experiments with acetone as the sensitizer ($E_{\text{Triplet}} = 350 \cdot 10^3$ joule $\cdot$ mol$^{-1}$) therefore do not reflect conditions in the environment. Sensitized reactions should play a relatively insignificant role in aquatic systems as in most cases both sensitizer and acceptor are present in very low concentrations. In addition, an effective quencher, oxygen, is normally always present in excess. Model calculations have shown that, owing to the above parameters, no noticeable contribution to the abiotic breakdown of organic chemicals in the environment can be expected from sensitized photodegradation in most aquatic systems (Coutant et al., 1979), but adsorption on to a sensitizer may negate this argument which is based on bimolecular collision theory (see Roberts et al., 1981).

### 3.1.3.4 Indirect Photodegradation and Oxidation

Apart from photo-oxidation, in which electronically excited molecules react with oxygen or oxygen containing compounds, thermal oxidative processes occur in water in which reactive oxygen species function as oxidants. When such oxidants have been generated photochemically, their reaction is spoken of as indirect or secondary photodegradation.

Singlet oxygen is an important reactive species in water. It is formed by the transfer of energy from naturally-occurring sensitizers to oxygen. The concentration of singlet oxygen in natural waters is variable and can amount to $2 \cdot 10^{-12}$ mol l$^{-1}$ in moorland water (Zepp et al., 1977). The reactivity of singlet oxygen with organic compounds varies widely. Compounds which contain double bonds are particularly susceptible to singlet oxygen reactions leading to the formation of peroxides or cycloaddition products depending on the substrate. Singlet oxygen also plays a role in the oxidation of sulphur or sulphides to sulphoxides. Phenols and polycyclic hydrocarbons are also degraded through this type of oxidation reaction.

Mill et al. (1980a) have proposed a test for determining the reactivity of test substances with singlet oxygen. The dye, rose bengal, is used as sensitizer for singlet oxygen formation. A determination of the breakdown of the test substance is carried out simultaneously with tests on a reference substance. The authors propose that this screening test be applied to substances which are expected to degrade via this pathway.
ABlOTIC CHEMICAL CHANGES IN WATER

The peroxy radical, RO₂, is another oxidant occurring in natural waters. RO₂ radicals can be formed by chain reactions from organic compounds, such as humic acids, naturally present in water. Light energy and singlet oxygen generated from natural sensitizers often act as initiators (Mill et al., 1978). RO₂ radical concentrations of 10⁻⁸–10⁻⁹ mol · l⁻¹ have been found in natural waters (Mill et al., 1980c). This radical reacts primarily through hydrogen abstraction, albeit a very slow reaction in many cases, and through addition to double bonds. Some classes of organic compounds are sufficiently reactive with RO₂ that they can be effectively degraded in the environment by this radical. Phenols, aromatic amines, hydroquinones and thiol derivatives are, for example, susceptible compounds (Mill et al., 1980a).

It is possible to estimate the reactivity of certain organic compounds with RO₂ radicals using laboratory experiments. Two procedures have been proposed (Mill et al., 1980b): one for the oxidation of C-H bonds and another for the usually rapid oxidation of phenols, aromatic amines and thiols. A water soluble chain initiator such as azo-bis-(2,2′-carboxymethyl-propane) serves as the primary radical source. The concentration of these two oxidants in natural waters is very low (10⁻¹⁴ mol · l⁻¹ for RO · and 10⁻¹⁷ mol · l⁻¹ for OH) (Mill et al., 1980c; Hendry and Mill, 1980). Therefore, in spite of their higher reactivity, RO and OH radicals cannot be expected to make a major contribution to abiotic degradation in aquatic systems (Hendry and Mill, 1980).

The irradiation of titanium dioxide particles suspended in water liberates electrons from the conduction band. These can then react with oxygen to give O₂⁻ ions, or, for example, cause a reductive dechlorination (Carey et al., 1976). However, this seems to be a special case, in that the low electron emission energy observed in this semiconductor does not reflect the general conditions associated with sediments occurring in the environment.

3.1.3.5 Anthropogenically Induced Transformations of Organic Compounds in Water

In the chlorination of water for drinking purposes, the chlorine can react with organic compounds dissolved in the water producing undesired chlorinated products. Depending upon reaction conditions, these chlorination reactions can either be radical or ionic in nature. They lead, to a certain extent, to the breakdown of organic substrates with the formation of low molecular weight chlorohydrocarbons such as chloroform (Rook, 1974; Bellar et al., 1974).

Naturally occurring organic compounds such as fulvic acids, and even chemicals such as halogenated phenols and anilines, comprise sources of low molecular weight chlorohydrocarbons in water (Rook, 1977; Hirose et al., 1982). An example of a chlorine substitution leading to an undesirable product is the reaction of biphenyl producing monochlorobiphenyl. This
reaction has been studied experimentally under conditions simulating those of drinking water chlorination (Snider and Alley, 1979).

The reaction of chlorine in aqueous media is pH-dependent. Molecular chlorine is only capable of acting as a strong chlorinating agent in acidic solution. Normally chlorine in water forms hypochlorous and hydrochloric acids. Undissociated hypochlorous acid is a moderately strong chlorinating agent whereas the hypochlorous anion has only very weak reactivity. Nevertheless, chlorination reactions are also observed in weakly alkaline solution where \( \text{Cl}_2\text{O} \), for example, is formed in small quantities (Snider and Alley, 1979).

Under the additional influence of light energy, homolysis of the hypochlorous acid produces \( \text{OH} \) and \( \text{Cl} \) radicals and initiates radical chain reactions, during the course of which oxidative as well as chlorinating cleavage and substitution reactions occur (Oliver and Carey, 1977).

If the chlorinated water contains bromide ions, these are oxidized to hypobromous acid which acts as a brominating agent. Depending on the quality of the water used, treatment with chlorine can lead not only to chlorinated substances but also to bromine derivatives (Sweetman and Simmons, 1980; Rook, 1974).

If ozone is used to sterilize and purify water for drinking purposes, compounds containing double bonds are attacked. The degradation and mineralization of other organic material can also occur due to the formation and reactions of radical oxidants, particularly under the additional influence of UV light (Kuo et al., 1977). Ozone treatment prior to breakpoint chlorination leads to a rise in the concentration of low molecular chlorohydrocarbons in drinking water (De Greef, 1978).

Irradiation with high-energy UV radiation is another effective method for the sterilization of drinking water. When sufficient oxygen is present, such treatment often leads to the mineralization of any organic compounds present.

In terms of quantities of products produced these transformation processes certainly play only a minor role in the total degradation in aquatic systems. However, as they directly affect the quality of drinking water, these reaction pathways are of major significance to humans and must therefore receive commensurate attention.

3.1.4 POSSIBILITIES FOR A COMPREHENSIVE ESTIMATION OF MOBILITY AND DEGRADATION IN WATER

3.1.4.1 Model Ecosystems

The transport and breakdown behaviour of chemicals in water may be estimated in total from experiments carried out in model ecosystems. These are experimental procedures in which highly simplified ecosystem conditions
are simulated in an artificial system containing natural water or a similar solution. Additional transport and degradation parameters can be evaluated by the inclusion of sediment, appropriate air movement factors and a light source which simulates sunlight. Such artificial ecosystems range in size and complexity from a 3-l container containing a simple aquatic food chain (Metcalf and Lu, 1973), to very detailed simulation systems in water tanks over 5 m³ capacity (Sanders and Falco, 1973).

Experiments with model ecosystems estimate abiotic and biochemical degradation together. It is normally not generally possible to differentiate the individual contribution from the two degradation routes.

Within the limited conditions of the model, experiments in artificial ecosystems can provide preliminary data on environmental behaviour of a chemical. The tendency of a compound to biodegrade and to bioaccumulate can be estimated particularly well. Laboratory tests on biodegradation employ only a relatively small portion of the natural microbial community and thus offer no decisive advantages over experiments in model ecosystems except that loading of the chemical can be strictly controlled. In contrast, when comparing tests of abiotic degradation, the limits of model ecosystems are more evident. Hydrolysis, for example, can only be followed at a single pH value rather than be assessed for a range of values encompassing various environmental situations. A valid simulation of sunlight in model systems is also difficult due to the problem of establishing a reliable cut-off at lower wavelengths as is done in laboratory tests. Controlled laboratory determination of quantum yield and subsequent calculation of the environmental half-life are therefore generally preferable to model ecosystem results.

Of the various mechanisms of abiotic degradation, the relevance of photodegradation is particularly difficult to assess, as the interaction of substance with radiant energy can be modified in many ways (see Section 3.1.3.2). Experiments in model ecosystems are helpful in this regard by indicating the comparative importance of this degradation pathway.

### 3.1.4.2 Estimation of Environmental Behaviour from Laboratory Data and Properties of the Substance

The significance of individual transport or degradation pathways for the environmental behaviour of organic chemicals can be estimated from laboratory tests and physicochemical data.

Laboratory data must be viewed in total in order to obtain a comprehensive picture of transport and degradation events. Two techniques are available for such a synthesis.

1. A mathematical integration of experimental or calculated degradation and transport rates, including input rates of the test compound where
possible (e.g. see Branson, 1978; Haque et al., 1980; Mill, 1980; Roberts et al., 1981).

(2) A listing of laboratory data, physico-chemical data and calculated coefficients of the ecotoxicological profile analysis type (Korte et al., 1978). This type of assessment is based upon comparisons to reference standards, for which good experimental and field data is available allowing an accurate description of the behaviour of the compounds in various aquatic systems.

The advantage of the latter method is that physico-chemical data can be used as well as dynamic parameters. A mathematical transformation of this data (with the aid of empirical correlations) is often unnecessary.

The following properties and constants of a chemical are related to its transport and degradation behaviour in water and should be included in a comprehensive assessment:

1. Water-solubility.
2. Vapour pressure.
3. Partition coefficient, octanol/water.
4. UV absorption.
5. Effect on the surface tension of aqueous systems.
6. Ability to form complexes.
7. Ionizability.

Additional properties are required for water-insoluble compounds:

1. Particle size.
2. Density.
3. Viscosity.

An estimation of the significance of abiotic degradation of a compound in water is generally only possible when data on transport behaviour and biodegradation are also available.

### 3.1.5 SUMMARY AND CONCLUSIONS

The most important demonstrated abiotic degradation pathways in water are hydrolysis, direct photodegradation and radical oxidation. These reactions can be simulated in laboratory experiments, for which conditions should be selected to correspond to those in the environment. When the reaction half-life is shorter under laboratory conditions than under environmental conditions, this result should be established to be due to quantitative and calculable effects (as far as possible) and not to some unaccounted factor which would negate the extrapolation of findings to the environment.

Substances can be compared with respect to their abiotic degradability when test conditions are standardized. Such laboratory tests thus provide a
measured of the specific behaviour of a chemical under conditions which do not mimic the natural environment but approximate important boundary conditions. Neither accepted test methods nor experimental research can possibly simulate the total multitude of reaction conditions operable in the aquatic environment.

3.1.6 REFERENCES


