

Review

# The Importance of Degradation in the Fate of Selected Organic Compounds in the Environment. Part II. Photodegradation and Biodegradation

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## Abstract

Compounds characterized by a slow degradation rate in the environment, i.e. resistant to biodegradation, and photolysis processes, are classified as persistent and have often been considered as potential environmental problems. A more exacting approach recognizes that a compound released to the environment has a tendency to accumulate in one medium more than in others. Hence, partitioning, transport, and transformation rates of any particular compound will differ in each medium. Degradation processes in the dominant medium (where the compound is preferentially accumulated) are expected to have more effect on overall persistence of the measured compound than degradation processes in the other media. Photodegradation and biodegradation are the degradation processes which can naturally clean up the environment. Biodegradation is expected to be the major mechanism of loss for most chemicals released into the environment. In this study, photodegradation and biodegradation processes of selected organic pollutants in different media have been reviewed.

**Keywords:** organic pollutants, photodegradation, biodegradation, products of degradation

## Introduction

Persistent organic pollutants (POPs) can cause serious problems in various environmental compartments due to their toxicity, persistence and bioaccumulation. Depending on the environmental compartment in which organic compounds are present (e.g. soil, benthic sediments, surface and ground waters), they can undergo slow changes resulting from chemical, biological or photochemical reactions. Photodegradation and biodegradation are major degradation processes which can naturally clean up the environment. Photodegradation, as a chemical reaction that occurs under the influence of photons or light, may take place in the atmosphere and on the surface of either water or soil, where as it does not occur in benthic sediments and deep

layers of soil. The intensity of UV radiation depends on many factors, among others, a time of the year, a time of the day, latitude, height above the sea level, air density, cloud cover or the size of the ozone hole [1]. Biodegradation is a multi-step process, which is taking place in the presence of a number of microorganisms that often act synergistically. The range and rate of biodegradation processes depend on several factors such as the composition and activity of bacterial flora, the properties and "age" of a pollutant, the content of nutritive ingredients and physico-chemical properties of the medium in which the reactions occur [2-4].

## Photodegradation

Sunlight reaching the Earth has a wavelength of over 286.3 nm [5]. The majority of UV rays are absorbed in the surface water layer (down to a 2 m depth). However, they

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can reach deeper depths under the condition that light penetrates there. When discussing photochemical reactions it has to be pointed out that there are two types of processes: a direct photolysis and an indirect photolysis [6].

*Direct photolysis* is a process in which molecules get excited by the absorption of a photon, and that results in a chemical reaction, usually oxidation. Photolytic potential mainly depends on the degree of overlap between the UV/VIS absorption spectrum of the compound and the emission spectrum of the beam of sunlight in the range 290-750 nm. The direct effects of UV irradiation include transformation of organic compounds into other substances, breaking of chemical bonds, or even complete degradation of organic substances. Also, UV radiation causes the dissociation of oxidizing compounds and the formation of highly reactive radicals that are capable of degrading organic pollutants [7].

*Indirect photolysis* of substances occurs through a reaction with OH-radicals, ozone or  $\text{NO}_3$ ; these three chemicals are considered the most important photo-oxidizing agents present in the atmosphere. The number of reactive radicals, such as OH or free oxygen, changes during a 24-hour cycle, starting with zero radicals at night and reaching a maximum at noon. Over 90% of organic compounds occurring in the gaseous phase of troposphere undergo transformations resulting from the reactions with OH-radicals [8-10].

The mechanism of radical formation through photolysis consists of several stages. Firstly, absorption of a quantum of energy (i.e. photon) by a molecule, takes place. Then breakage of chemical bonds within the molecule occurs as a result of irradiation of sufficient energy (the energy increases as the wavelength decreases;  $E=hc/\lambda$ ). This step is followed by the formation of very reactive intermediate forms of radicals, i.e. OH, OOH.

### Photodegradation of Organic Compounds in Aqueous Media

The phototransformation of a compound in surface water may result from light absorption by the pollutant itself (direct photolysis) or may be photoinduced by the dissolved natural organic matter or nitrate ions present in water, as these chromophores are known to photoproduce reactive species (indirect photolysis). In an aquatic environment, the processes of direct and indirect photolysis occur concurrently. The presence of microorganisms, algae or humic substances accelerates photochemical reactions due to the fact that these components are capable of absorbing sunlight. Some non-ionic organic compounds, particularly pesticides, undergo photodegradation much faster in the presence of photosynthesising microorganisms [11]. Based on the results obtained by Zepp and Schlotzhauer [10], it has been concluded that the majority of PAHs get photolyzed much faster in the presence of algae.

According to Wu et al. [6] phenol degrades through direct photolysis, thermal disassociation and the reaction with hydroxyl radicals  $\cdot\text{OH}$ . The rate of phenol degrada-

tion increases with a decreasing value of pH and an increasing oxygen concentration in water. The presence of intermediate products of the reaction (i.e. hydroquinone, p-benzoquinone and catechol) proves that  $\cdot\text{OH}$  takes part in the process of phenol degradation according to the scheme presented in Fig. 1.

The investigations of Jongki et al. [13] showed that the main photodegradation products of pentachlorophenol, a compound commonly used as herbicide, insecticide and for treating wood, are substances that form during the oxidation by hydroxyl radicals, as well as products originating from the reduction of chlorine atoms in *ortho* and *para* configurations. Tetra-, tri- and dichlorophenols are typical products of successive dechlorination of pentachlorophenol. During the reactions of dehydroxylation, chlorination or dechlorination, hexachlorobenzene and pentachlorobenzene are formed and these, in turn, are oxidized to hexachloroquinone and tetrachlorocatechol. Further oxidation leads to the formation of 1,2,4-trihydroxytrichlorobenzene. Such degradation products are also formed when the reactions take place in organic solvents, i.e. acetone. However, the products are absent in the presence of oxidizers, such as  $\text{TiO}_2$  or  $\text{H}_2\text{O}_2$ . This proves that depending on photolytic conditions, various degradation products can originate. Besides the main photolytic products, the presence of polychlorinated diphenylethers (PCDPEs) and polychlorinated dibenzo-p-dioxin (PCDDs) has also been observed.

Photolysis plays a significant role in the process of transformation and decomposition of polychlorinated

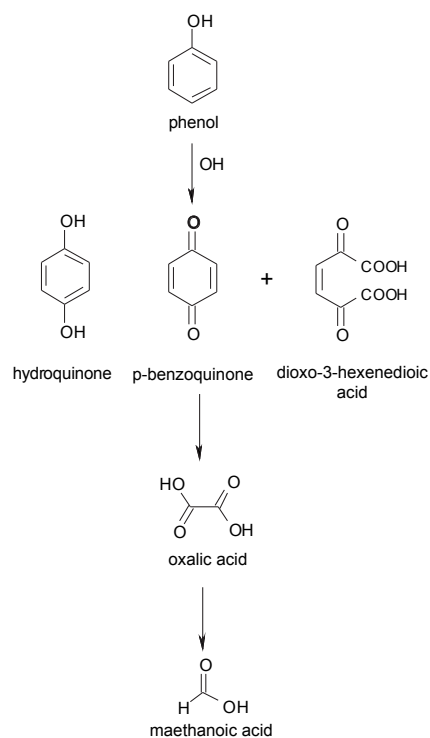


Fig. 1. Schematic presentation of phenol degradation in aqueous solutions [12].

dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in aqueous solutions [14, 15]. These compounds are characterized by high persistence, toxicity and a tendency to bioaccumulate in live organisms. The rate of photochemical reactions depends on the number of chlorine atoms in a compound. Therefore, the more C-Cl bonds the slower the rate. MeeKuyung and O'Keefe [14] investigated degradation of selected PCDDs and PCDFs during exposure to the laboratory UV light (300 nm) and to sunlight in situ. The obtained results show that, for the wavelength  $\lambda=300$  nm, the analytes from the PCDF family degrade faster than PCDDs. The rate of photolytic degradation of PCDF analytes in clean water is higher than in an aqueous medium containing acetonitrile while in the case of PCDDs, the opposite is true. The underlying cause of this phenomenon most likely lies in the structure and polarizability of the compounds. The compounds from the PCDF family contain in their structure only one oxygen atom and those results in a better polarizability as compared to PCDDs. They are also characterized by a higher reactivity in clean water than in the less polar aqueous medium containing acetonitrile.

Photolysis is a major abiotic degradation process (chemical oxidation and photooxidation) for many PAHs in the aquatic environment. Generally, compounds with higher molecular weight and more condensed aromatic rings have a higher rate of photolysis than smaller and less condensed ones. In the case of phenanthrene and anthracene, the molecular structure has been shown to be of importance, with typically lower photoreactivity in non-linear molecules [16, 17]. According to Lehto et al. [18], the photodegradation of PAHs, which is assumed a preliminary process after which the microbial decomposition of compounds occurs, causes the formation of partially oxidized, intermediate compounds that are more susceptible to biodegradation than the parent compounds. Quinones are intermediates in the environmental oxidation of PAHs. Anthracene readily oxidized with the formation of 9,10-anthracenedione (anthraquinone) as the primary product [19]. Photolysis of benzo[a]anthracene and benzo[a]pyrene in water is slowed down considerably when amended with humic acids [20]. The proposed explanation for this observation was that humic substances caused a quenching or scavenging of PAH-excited states, free radicals or other excited state complexes that participate in the photochemical reaction [21].

The principal degradation pathways for pesticides involve photolysis, hydrolysis, dehalogenation and oxidation. Photochemical degradation is one of the major transformation processes and one of the factors controlling the fate of pesticides in the environment. Photodegradation can destroy pesticides on foliage, on the soil surface, and even in the air. Considering the chemical structure, pesticides have been classified into organic and inorganic compounds. Factors that influence pesticide photodegradation include the intensity of the sunlight, properties of the application site, the application method, and the properties of the pesticide.

Vialaton and co-workers [22] studied the photolysis of propiconazole in pure water, in water containing humic substances and in natural water. Propiconazole was photodegraded in solar light. The phototransformation was faster by about 30% in natural water than in pure water.

Organic pesticides comprise, among others, phospho- and chloroorganic compounds, the derivatives of phenoxyacetic acid, triazine and many others [23, 24]; they are present in all the environmental compartments. When washed out from soil, they are transferred not only to the rivers, lakes and oceans, but also to ground waters. The photochemical pathways of fungicides (e.g. N-dichlorofluoromethylthio-N,N'-dimethyl-N-phenylsulfamide) in the samples of natural waters, i.e. seawater, riverine and lake water, and in distilled water have been investigated by Sakkas et al. [25]. Based on the conducted experiment, it has been concluded that the degradation of dichlofluanid is slower in natural water than in distilled water. It was possible to obtain the following ranking of degradation rates for different water bodies: lake water < riverine water < seawater < distilled water. Such a paradigm shows a strong interrelation between the level of photodegradation and the presence and concentration of dissolved organic matter in particular matrices. With an increasing concentration of total organic carbon (TOC) in natural waters, the rate of photodegradation decreases. Microorganisms and sediment particles suspended in water cause the dispersion of light and, therefore, can remain a certain barrier for light-penetrating deeper water layers. The photolysis in samples exposed to the light under laboratory conditions was faster than in those subjected to direct sunlight. This resulted from the fact that the sunlight intensity varied in dependency on a time of the day and atmospheric conditions while the radiation intensity in the laboratory was constant during the entire experiment. Nevertheless, in all cases the presence of new compounds, possibly the products of degradation, was observed. Four of the compounds have been identified as aniline, dimercaptosuccinic acid (DMSA), dichlorofluoromethane and n-dichlorofluoromethylthion-aniline (Figure 2).

Most of the photolysis studies [26, 27] have used natural sunlight, so it is unclear what wavelength range of light actually contributes to the photolytic reaction. Hirahara and coworkers [28] compared the photolysis of fenthion and disulfoton (organophosphorus pesticides) in liquid and solid – phases with different source of visible light and ultraviolet to estimate the extent of their photodegradation. They concluded that UV wavelength of light is capable of causing the photolysis of fenthion and disulfoton. UVB is primarily responsible for the photodegradation in the environment, and that fenthion is more readily degraded than disulfoton.

The photooxidation rate changes depending on the solvent. The rate constant obtained for fluorene decreased in the order of dichloromethane > acetonitrile > methanol > acetonitrile/water (70/30) > acetonitrile/water (50/50); nonpolar solvents generally gave higher values than the

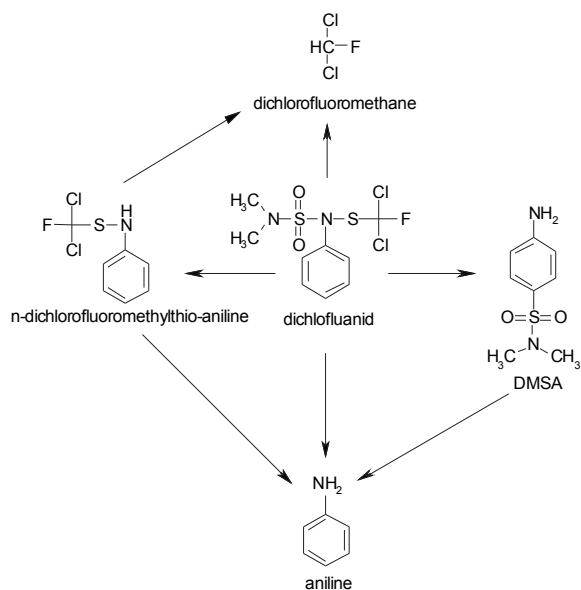


Fig. 2. Photodegradation pathway of dichlofluanid in aqueous solution [25].

polar ones. This is mainly due to a difference in the solubility of oxygen [29].

Recently, the review, which accounts for current knowledge about the distribution, accumulation, and chemical/photochemical transformations of persistent, bioaccumulative, and toxic compounds in water ice, especially in the connection with polar regions and atmospheric cloud particles has been published by Klán and Holoubek [30]. According to the authors, ice photochemistry might play an important role in the chemical transformations in cold ecosystems and in the upper atmosphere, particularly now when the ozone layer is partially depleted. Photoreactions resembling liquid phase photochemistry are expected in a quasi-liquid water layer on the surface snow (ice) grains at higher (sub-zero) temperatures, especially when the organic substances are more hydrophilic (i.e. water soluble). Photochemical degradation of 4-nitrophenol in ice pellets is a good example as presented by Dubowski and Hoffmann [31]. They found similar photoproducts, hydroquinone, benzquinone, 4-nitrosophenol etc., as known from 4-nitrophenol photolysis in aqueous solutions. The results suggest a similar mechanism for the decomposition in both liquid and solid states (Figure 3).

The possibility that ice photochemistry can lead to the formation of new and unexpected organic compounds of high-environmental risk, supported by some laboratory experiments, brings new insight to the problem, which will be the result of global warming processes if ice melts.

### Photodegradation of Organic Compounds in the Soil

The concentrations of hazardous substances in water or atmosphere decrease relatively fast as a result of mixing and dilution while many organic pollutants tend to accu-

mulate in soil. Non-ionic and non-polar hazardous organic compounds tend to adsorb by humic substances. They accumulate in the surface layer of soil because most of the organic matter is present there. An organic compound can undergo photolysis after adsorption by colloidal substances in soil, and also when it is present in the surface layer of soil exposed to light [32]. Therefore, photochemical reactions in soil are only and exclusively restricted to its surface; they extend to the maximum depth of 1 mm [11]. Non-biological degradation, i.e. photodegradation, occurs concurrently with the reaction catalyzed by microorganisms. Therefore, the information in reference to photochemical reactions in soil is rather scant.

Romero et al.[33] investigated degradation of phenoxyacetic acids (i.e. mecoprop and dichlorprop) in soil samples of different humidity and organic matter content. Based on the conducted investigations, it has been concluded that the removal rate of dichlorprop (DCPP) and mecoprop (MCP) depends on soil humidity, i.e. the rate is much slower in dry soils. The photochemical decomposition of MCP occurs much faster than in DCPP, which might likely be explained by different abilities of these compounds to be adsorbed by soil.

### Biodegradation

Biological decomposition of persistent organic pollutants by microorganisms is one of the most important and effective ways to remove these compounds from the environment. Usually, the biodegradation of organic compounds is a multi-step process, which is taking place in the presence of a number of microorganisms that often act synergistically. The biodegradation rate in real aquatic environment depends on characteristics of the aquatic system, the presence of particulate matter, concentration of inorganic and organic nutrients, temperature, oxygen concentration, redox potential and adaptation of the microbial population. In soil, the range and rate of biodegradation processes depend on several factors such as soil temperature, soil moisture content, the composition and activity

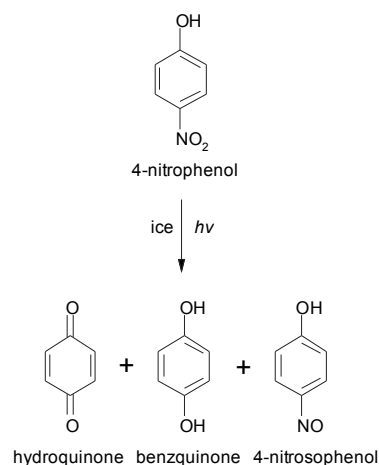


Fig. 3. Photochemical degradation of 4-nitrophenol in ice pellets.

of bacterial flora, the properties and “age” of a pollutant and the content of nutritive ingredients [2, 3].

Microorganisms, in comparison to other organisms, have a particular predisposition to adapt to novel environmental conditions and the ability to utilize compounds that are not the products of their own metabolism, as substrates needed for energy production and structure building. In general, microorganisms can be divided into autotrophic that use carbon dioxide as a carbon source, and heterotrophic that obtain carbon from decomposition of organic matter and man-made organic substances. The processes in the organic compounds take place due to direct contact with the microbial cellular enzymes.

One molecule of enzyme can catalyze decomposition of millions of organic molecules per minute [34, 35]. The reactions mediated by microorganisms are, to a large degree, similar to those occurring in higher organisms. Therefore, the aromatic compounds undergo epoxidation and hydroxylation, the aliphatic ones are oxidized and degraded through  $\beta$ -oxidation pathway, and the nitro-organic derivatives are metabolized with the use of nitroreductases. Microorganisms can also mediate the processes that the higher organisms are not capable of, e.g. decomposition of aromatic ring or dehalogenation.

In general, there is a relatively large variety of microorganisms in the natural environment; a higher diversity has been observed in the microbial biocenoses associated with sediments than in ground waters originating in formations of large pore size and inhabited by mobile microorganisms. Microorganisms residing in sediments are sedentary, permanently bound and living in pores of small diameter. The characteristic morphological types are gram-negative rods, among others, aerobic rods from the genera *Pseudomonas*, *Flavobacterium*, *Azotobacter* and *Rhizobium*, non-obligatory anaerobic species *Aerobacter aerogenes*, and anaerobic species from the genus *Desulfovibrio*. From among the gram-positive bacteria, typical for this environment is the genus *Arthrobacter*, as well as bacterial spores from the aerobic genus *Bacillus* and anaerobic genus *Clostridium* [36].

### Biodegradation of Organic compounds in Soil and Benthic Sediments

Soil is a mixture of organic, mineral, gaseous and liquid components inhabited by numerous microorganisms. Organic matter in soil consists of the remnants of decomposing plants and humic substances. The mineral components of soil are particles of weathering rocks, silt and hydrated oxides of Al. Organic compounds are decomposed by microorganisms that live in soil; however, the rate of decomposition depends on the properties of an organic substance, microbial genotypes, pH, nutritive properties of soil, soil temperature, soil moisture content and soil adsorption characteristics. Enzymes cause microbial decomposition of substances, and it generally occurs after an initial latency period during which the microorganisms

adapt to novel substratum. In many cases, the reactions taking place in soil are similar to those occurring in sediments, although usually only the surface layer of sediment contains oxygen. Most of the sediment constitutes the anaerobic compartment [32].

Polycyclic aromatic hydrocarbons get transferred into the environment as a result of the incomplete combustion of organic substances at high temperature [37]. The ability of microorganisms to degrade polycyclic aromatic hydrocarbons depends on the number of aromatic rings in a given compound. Microorganisms can decompose compounds with 2 to 4 benzene rings and, at the same time, use the process as a carbon source. A larger number of rings, i.e. 5 to 6, give the compound higher resistance to microbial “attacks” [38, 39].

The research of degradation processes of selected PAHs by various strains of aerobic bacteria has been described by Yuan et al. [40]. Experiments which were conducted for 5 different PAHs being decomposed in a mixture separately showed that phenanthrene, acenaphthene and pyrene were completely degraded within 28 hours, 10 days and 12 days, respectively; at the same time, the content of anthracene and fluorene practically did not change. After mixing all the compounds together, a decrease of phenanthrene, acenaphthene and pyrene biodegradation was observed while the rate of the process for anthracene and fluorene showed an increase. This has proven that the compounds of lower molecular weight degrade much faster as compared to compounds characterized by high molecular weight. The same authors investigated the subject of phenanthrene biodegradation in riverine sediments [41]. The obtained results have indicated that the phenanthrene biodegradation rate varies depending on the values of pH and temperature, with the optimal rate reached for 30°C and pH=7.0. The additional substances, such as sulphates and phosphates, did not show an effect on the degradation rate.

Based on scientific information, it has been concluded that biological treatment of soil in order to eliminate PAHs of lower molecular weights (e.g. naphthalene, phenanthrene and pyrene) is very effective because many microorganisms capable of utilizing such compounds as an energy and carbon source were identified and researched (Fig. 4) [38, 39, 42-44].

Juhasz et al. [42] have investigated the biodegradation of benzo(a)pyrene, dibenzo(a,h)anthracene and coronen, all compounds of high molecular weights, by using a strain of *Burkholderia cepacia* (VUN 10,001). The used bacterial strain degraded PAHs with 5 and 7 aromatic rings; however, the rate of the process was much lower as compared to that for pyrene. A noticeable 20-22% decrease of benzo(a)pyrene and dibenzo(a,h)anthracene content was observed after only 63 days of incubation. In case of coronen, after 63 days, its concentration decreased by 75%.

Aerobic degradation of PAHs in sediments has been extensively documented by Cullen et al. [46]

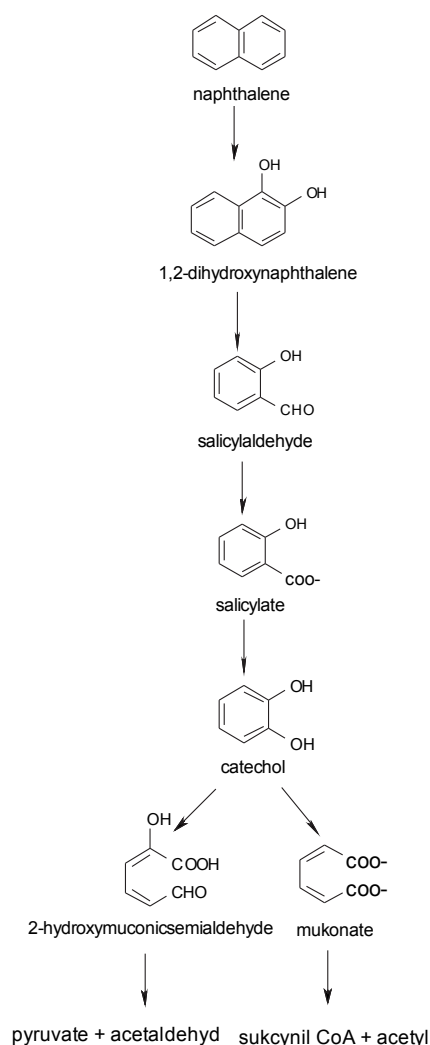


Fig. 4. Schematic pathway of naphthalene degradation by bacteria from the genus *Pseudomonas* under aerobic conditions [45].

and Geiselbrecht et al. [47]. Verification of anaerobic degradation of PAHs under nitrate-reducing conditions has been presented by Bregnard et al. [48] and Langenhoff et al. [49]. Chang and co-workers [50] suggest that anaerobic microorganisms might have greater potential for organic-pollutant detoxification in the environment. Comparison of phenanthrene degradation under three reducing conditions was done and it has been the order of phenanthrene remaining for sediment sample are: nitrate-reducing conditions > sulfate-reducing conditions > methanogenic conditions. It has also been found that additional acenaphthene and phenanthrene was completely degraded in sediments within a 56-day incubation, while pyrene, fluorene, and anthracene degraded only 4.0, 28.0 and 48.7% within a 56-day incubations period. High to low degradation rates were phenanthrene → acenaphthene → pyrene → fluorene → anthracene. According to Walton and Anderson [51], PAH bioavailability and biodegradability depend primarily on the complexity

of their chemical structures and corresponding physicochemical properties.

Biodegradation of polychlorinated biphenyls (PCBs) is a multi-step process that involves aerobic and anaerobic bacteria. Anaerobic bacteria are capable of decomposing compounds containing several chlorine atoms while anaerobic bacteria only degrade compounds with one or two chlorine atoms. The first step of the process is degradation of polychlorinated compounds, during which bacteria do not use PCB as a carbon source, but rather as an electron acceptor. The derivatives with one or two chlorine atoms, originating in the process, undergo further decomposition through breaking of the aromatic ring in the presence of aerobic bacteria. The ensuing reactions lead to the production of inorganic chlorine, carbon dioxide and water, as stated by Müller and Lingens [52]. Fig. 5 shows a generalized pathway of microbial degradation of PCBs.

Immobilized cells of *Pseudomonas* sp.2 are able to degrade di-, tri-, and even tetrachlorobiphenyls. According to Komancova [53] 52-99% of original PCBs was degraded after three weeks. For all tested congeners, chlorobenzoic acids were found as degradation products. The most common and the most investigated pathway of PCB transformation is 2,3-dioxygenase attack starting by the oxidation of less chlorinated ring [53]. White rot fungi (*Pleurotus ostreatus*) had biodegradation ability of low chlorinated PCBs. *P. ostreatus* strains decomposed PCBs selectively with the preference for congeners with chlorine atoms in *ortho*>*meta*>*para* positions. Degradation efficiency decreased with an increasing number of chlorination [54].

The potential for the anaerobic degradation of three PCB congeners (2,3,5,6-CB; 2,3,4,5-CB and 2,3,4,5,6-CB) in sediments was investigated by Chang et al.[55]. According to the authors, intermediate 2,3,4,5-CB products were identified as 2,3,5-CB, 2,3,6-CB and 2,5-CB. For 2,3,5,6-CB intermediate products were identified as 2,3,6-CB and 2,5-CB. Dechlorination rates for PCB congeners were observed as (from the fastest to the slowest): 2,3,4-CB > 2,3,4,5-CB > 2,3,4,5,6-CB > 2,2',3,3',4',5'-CB > 2,2',4,4',6,6'-CB > 2,2',3,4,4',5,5'-CB > 2,2',3,3',4,4',5,5'-CB. The rates decreased for mixtures of the eight congeners. Dechlorination rates for three primary congeners under different reducing conditions occurred in the following order (from the fastest to the slowest): methanogenic condition > sulphate-reducing condition > nitrate-reducing condition. Under methanogenic and sulphate-reducing conditions, dechlorination rates were enhanced by the addition of lactate, pyruvate or acetate, but decreased as a result of the addition of manganese oxide or ferric chloride. Under nitrate-reducing conditions, dechlorination rates were decreased by the addition of lactate, pyruvate, acetate, manganese oxide or ferric chloride. The dechlorination of the three PCB congeners was affected by changes in pH, temperature and the presence of an electron donor or acceptor.

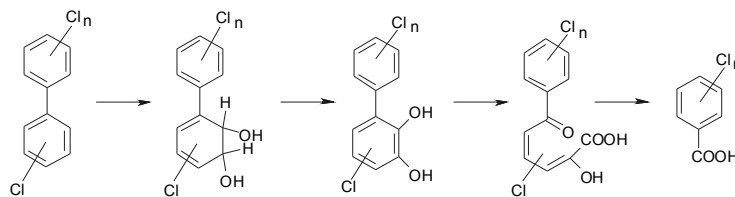


Fig. 5. Microbial degradation pathway of polychlorinated biphenyls [52].

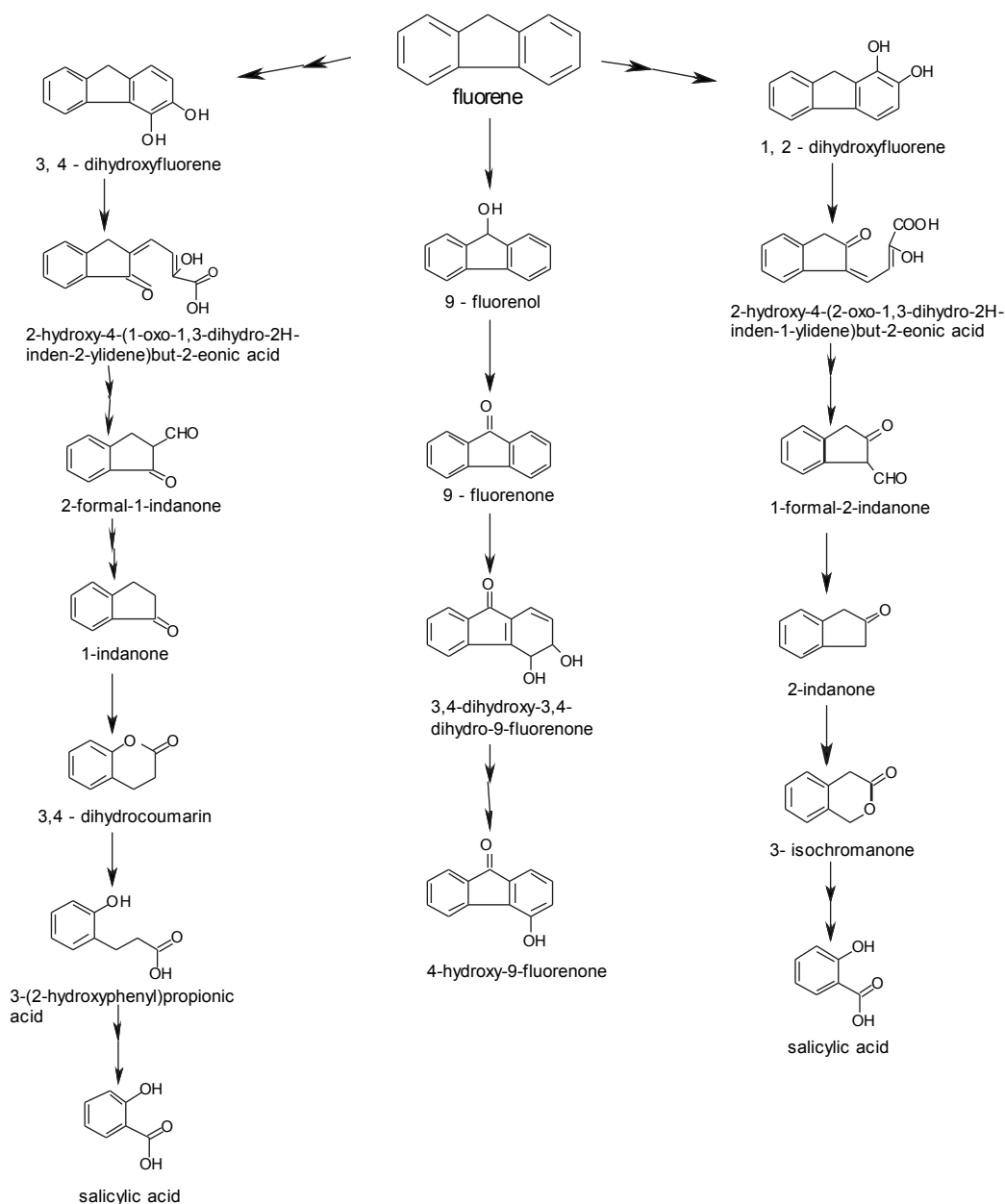


Fig. 6. Degradation pathway of fluorene [62].

### Biodegradation of Organic Compounds in Ground- and Surface Waters

Phenoxyacetic acids are herbicides widely used in agriculture. These compounds are selective because grains are resistant to their herbicidal properties while leafy

plants display sensitivity. Herbicides get into waters by means of diffuse run-offs from agricultural fields. Harrison et al. [56] investigated degradation rates, under aerobic and anaerobic conditions, in 3 herbicides, namely derivatives of phenoxyacetic acid, i.e. MCPA, present in groundwater. The experiments were conducted by using

ISM technique (*in situ* microcosms) [57, 58] while the final determinations were performed by HPLC. Based on the experimental results it has been concluded that during aerobic degradation all herbicides underwent complete decomposition. Under anaerobic conditions, in the course of 100-200 days of the experiment no changes in the content of selected phenoxyacetic acids were observed [56].

The degradation of sulfonylurea herbicide rimsulfuron and its major metabolites in freshwater was investigated by Martins et al. [59]. They investigated that in aqueous solutions, rimsulfuron is rapidly hydrolyzed into metabolite 1, which itself is transformed into the more stable metabolite 2. Metabolite 2 is more persistent ( $t_{1/2} = 8.1-55$  days, depending on initial concentration) and can present a potential danger to groundwaters.

The phenomena connected to degradation of polycyclic aromatic hydrocarbons in water have also been discussed in many studies. Microbial decomposition of selected PAHs in samples of water collected from wells was investigated by Ogawa et al. [60]. The compounds degraded almost completely within 3 days. The removal rates of particular PAHs have been ranked as follows: acenaphthylene > acenaphthene > 2-methylnaphtalene > 2-methylindene > 3-methylindene > lindane.

Garon et al. [61] investigated the degradation of fluorene by different fungal strains, isolated from soil, that have been known to effectively degrade PAHs. Water samples containing different fungal strains and contaminated with fluorene were incubated for 2 days, and later analysed using HPLC. Twelve of the investigated strains degraded 60% or more of fluorene; three strains from the family *Cunninganella* achieved 96% degradation. In all cases, the main products of fluorene degradation were 9-fluorenol and 9-fluorenone. Both newly formed products were identified based on a comparison of retention time and absorption spectrum against the standardized reference materials. The pathway of fluorene biodegradation is presented in Fig. 6.

Ravelet et al. [63] researched the degradation of pyrene by using white-red fungi. Forty-one fungal strains were isolated from the sediments contaminated with PAHs, and later identified and classified into several taxonomic groups, i.e. *Zygomycetes*, *Deuteromycetes*, *Dematiaceae* and *Sphaeropsidate*. Pyrene-containing samples were incubated for 2 days and afterwards the content of the remaining compound was measured. For 10 of the isolated strains a large decrease of pyrene was observed while *Zygomycetes*, particularly *Mucor racemosus*, has been recognized as the group most effective at pyrene decomposition. A *Penicillium crustosum* strain was the only one not capable of degrading pyrene at all. Among the 10 pyrene-degrading fungi nine have not been previously described in literature.

Gram-negative bacterium (strain MV1) has been used to degrade bisphenol A (BPA) in aquatic environment [64]. Two primary metabolites of BPA degradation by the strain MV1 have been found out: 4-hydroxybenzoic acid

and 4-hydroxyacetophenone in the major pathway, and 2,2-bis(4-hydroxyphenyl)-1-propanol and 2,3-bis(4-hydroxyphenyl)-1,2-propanediol in the minor. The rate of BPA degradation depends on bacterial counts of the samples.

The changes in the mutagenicity of fenitrothion during its biodegradation in solutions were investigated by Matsushita et al. [65]. Fenitrothion is completely decomposed within 12 days. The mutagenicity increased during anaerobic biodegradation, which was due to amino-fenitrothion, a metabolite formed during anaerobic biodegradation of fenitrothion. In the case of chlornitrofen, mutagenic metabolites were formed during anaerobic biodegradation, too [66].

## Conclusions

Natural attenuation processes, and particularly photodegradation and biodegradation, are complex as they involve bacteria, chemical reactants and transport of these species. Many experiments showed that biodegradation rates of PAHs, pesticides, phenoxyacids, PCBs phenols or even chlorinated solvents, might be fast (i.e. half lives of hours or days, under optimal conditions). However, much slower degradation rates were found in field studies. Despite this knowledge, degradation often relies on first order kinetic rates. In this paper we tried to overview data available on that subject.

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