CRITICAL REVIEWS

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PHOTODEGRADATION OF ORGANIC PESTICIDES IN THE ENVIRONMENT

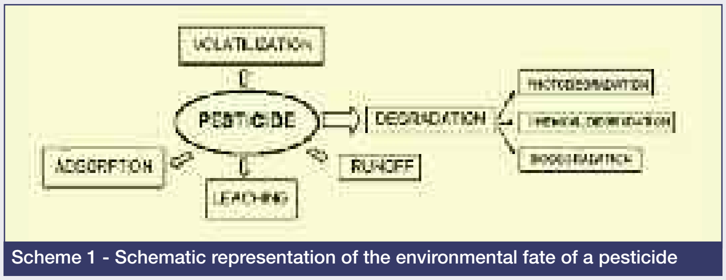
Reactions induced by absorption of light contribute to the degradation of many chemical compounds in the environment. A critical overview on the current research activity concerning direct and indirect photodegradation processes of organic pesticides in the aquatic environment and on soil is reported.

Photochemical reactions, namely reactions induced by the absorption of ultraviolet or visible light, play a crucial role in the environment. Life on earth depends on the influence that light has on chemical reactivity. Solar radiation promotes fundamental processes, which led to the development and evolution of life: photosynthesis in plants and photochemistry of the atmosphere are the best known examples. Light is furthermore involved in many reactions in surface waters and soil: phototransformation processes play an important role in the degradation of organic compounds, particularly in the case of poorly biodegradable pollutants.

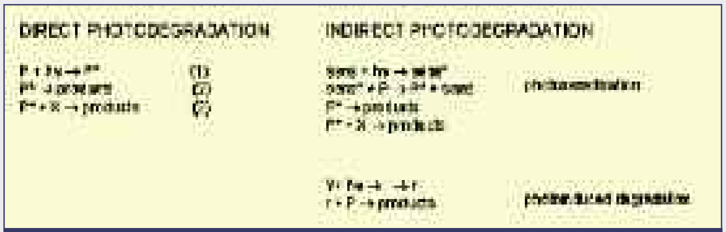
During the last decades the use of organic pesticides, mostly in agriculture, has greatly increased; it has been estimated that after application they are distributed among the major environmental compartments (atmosphere, soil, water and biota). In recent years, the scientific community has highlighted the adverse effects that their presence in water and food may have for human health and for the equilibrium of ecosystems and such concern is supported by results from monitoring studies.

It is therefore important to understand the environmental fate of pesticides in order to assess their potential exposure and associated risks for human health and the environment. The environmental fate of a pesticide, reported in Scheme 1, depends on three major types of processes, adsorption to the components of soil, transfer within the environment and degradation processes which break down pesticides into simpler and, generally, less toxic compounds; among the different transformation processes, biotic and abiotic, photodegradation in surface water and on soil induced by sunlight has been recognized as an important factor contributing to the fate of these xenobiotics, particularly for compounds characterized by poorly efficient hydrolytic and biochemical transformations.

The absorption of sunlight by both natural and anthropogenic chromophores can initiate a variety of environmentally important photochemical processes broadly classified into the two categories of direct and indirect photodegradation (Scheme 2). Direct photodegradation occurs



Scheme 1 - Schematic representation of the environmental fate of a pesticide



Scheme 2 - A simplified representation of processes involved in direct and indirect photodegradation, where P: pesticide, P*: pesticide in an electronically excited state, sens: sensitizer, X: other chemical species, Y: photoinductor (such as DOM, nitrates, Fe(III) complexes), r: reactive species

when a photon is absorbed by a compound leading to formation of an electronically excited species, which can react in a variety of ways to form stable products; the chemistry of an electronically excited chemical species can differ markedly from that of the ground-state, leading to different products than those formed in the dark. The reaction involved may be either intramolecular (process 2 in Scheme 2), leading for example to dissociation, ionization, isomerization, or intermolecular (process 3), including reactions with other chemical species or, in solution, with the solvent. The photostability of a compound is evaluated through the photoreaction quantum yield, which is defined as the ratio between the number of molecules that undergo phototransformation and the number of photons of light absorbed in the unit of time. In indirect photodegradation a photon is absorbed by a chromophore, other than the chemical species of interest, able to transfer its excitation energy to the chemical (photosensitization) or, alternatively, to form highly reactive species, such as hydroxyl and peroxyl radicals, singlet oxygen, superoxide anions, which can react with the compound of interest (photoinduced degradation); in indirect photoreactions an important role is played by humic substances, nitrate and carbonate ions, compounds of Fe(III).

Another important topic of environmental concern is the use of photochemical reactions for the detoxification of polluted water: some of the advanced oxidation processes (AOPs), which are based on oxidation reactions in order to transform organic pollutants in less toxic and more easily biodegradable compounds, employ photochemical reactions, involving UV photolysis either on its own or in presence of oxidising agents, such as ozone or hydrogen peroxide, or semiconductor materials [1]. Photochemical advanced oxidation processes (PAOPs) include photo-ozonation, photo-Fenton process, heterogeneous photocatalysis.

Interest in environmental photochemistry has grown enormously in the last decades due to legislative requirements and an increased public awareness with respect to environmental matters. It is now essential that we have as much information as possible about the fate of xenobiotic compounds in the environment, about not only their toxicity, but also the nature and toxicity of the products of transformation. Furthermore, there is a currently considerable interest in those methods with great potential for the destruction of pollutants.

The research area of environmental photochemistry is quite recent and has increased during the last decades. Thanks to new knowledge on photochemical mechanisms and the development of steady-state and pulsed irradiation methods, together with sensitive analytical techniques, study on the photochemistry of pesticides has proceeded from merely measuring the disappearance of a given compound to identifying the products and the pathways leading to them; at the same time investigations on the photodegradation processes under natural environmental conditions have been carried out. The aim of the present work is to review the current knowledge on the photodegradation processes of organic pesticides in the environment: a critical overview on studies concerning direct and indirect photoreactions, in the aquatic environment and on soil, is reported, outlining mechanistic aspects and evaluating the overall significance of the studies from an environmental point of view.

Photodegradation of pesticides in water and soil

Direct photodegradation

The direct photodegradation in the environment is a process restricted to those compounds that absorb wavelengths with $\lambda>290$ nm and its importance is affected by several factors: it depends on the overlap of the absorption spectrum of the pesticide with that of solar emission (Fig. 1) and on the quantum yield of the process; furthermore in the hydrosphere it can take place at a depth dependent on the transparency of water (for typical surface and marine waters the photochemical zone depth is 6-30 m [2]), while in soil it is limited to surface layers, up to approximatively 0.2 mm for direct photolysis [3].

The European Community legislation, concerning the placing of plant protection products on the market, states that physical and chemical properties of agrochemicals must be studied (Council Directive 91/414/EEC of 15 July 1991), including direct phototransformation processes in water, if molar absorption coefficients of compounds of interest are higher than 10 $M^{-1}xcm^{-1}$ at wavelengths ≥290 nm (Com-

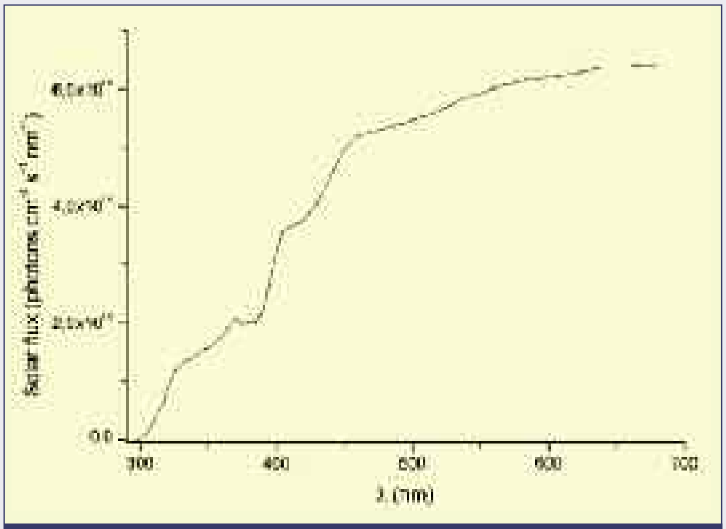
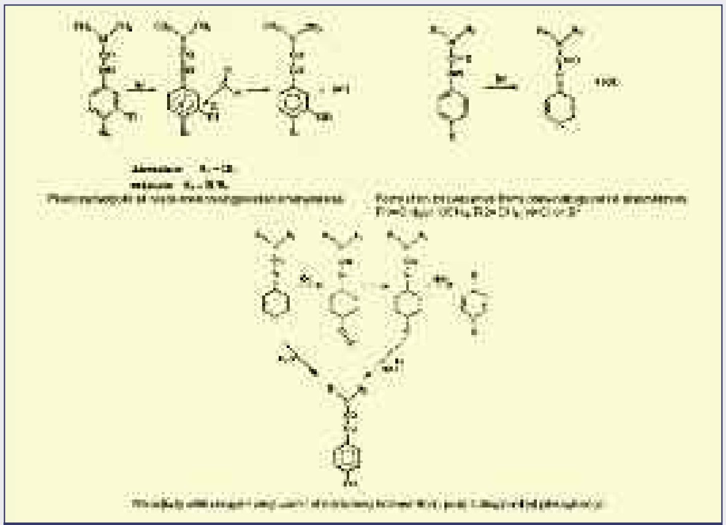


Fig. 1 - Actinic flux at the earth surface for a solar zenith angle of 40° (data from B.J. Finlayson-Pitts, Chemistry of the upper and lower atmosphere, Academic Press, 1999)

mission Directive 94/37/EC of 22 July 1994): these studies must include the identification of the photoproducts, the determination of the photochemical quantum yield as well as photochemical half-life, employing a light source that simulates sunlight. A detailed treatment of the theory and practice of determining kinetic rates and half-lives in the aquatic environment was first reported by Zepp [4]; the determination of quantum yields with monochromatic or polychromatic sources and in sunlight have been discussed [5, 6]. The software routine GCSOLAR, available on Environmental Protection Agency (EPA) website [7], allows us to compute, given the quantum yield of photodegradation and molar absorption coefficients of the pollutant at wavelength >280 nm, the direct photolysis rates and half-lives as a function of season, latitude, time-of-day, depth in water bodies and ozone layer thickness.

The first contributions on the photodegradation of pesticides in water were published in the early Seventies by J.R. Plimmer and R.G. Zepp in the USA. Since 1980 this theme has become a main topic of research also in Europe. Many laboratories have undertaken studies on the photodegradation of the main classes of pesticides, including organochlorines, organophosphorous, carbamates, triazines, pyrethroids, nitroanilines, amides, phenylureas and sulfonylureas. The direct and indirect photodegradation of some classes of pesticides have been reviewed [8]. Although the studies concerning the direct photodegradation of organic pesticides are numerous, there is a notable lack of detailed mechanistic studies on the photodegradation of pesticides under environmental conditions, including the identification of stable and short-lived intermediates involved.

The kinetic treatment of photochemical processes in aquatic environmental systems has been thoroughly discussed [4]: in optically dilute solutions, as is often the case for pollutants in natural waters, direct photodegradation proceeds by first-order kinetics, while, in a case where the pollutant absorbs all of the incident light, the rate of photoreaction becomes zero-order. Since the photodegradation rate depends on the intensity of the light source, kinetic constants or half-life values can be compared only if determined under identical experimental conditions: rate data taken from different research groups cannot be compared, due to differing light sources used. From an environmental point of view these values are significant only if obtained by means of the standardised method [4, 7]. The role of the solvent in phototodegradation processes has rarely been considered, although it has been demonstrated that the photochemical behaviour can depend from the medium: the particular influence of water on photochemical pathways has been showed for several classes of compounds, among which haloaromatics [9]. Despite this, many experiments, mainly when the compounds of interest are poorly soluble in water, are performed in aqueous mixtures of organic solvents; however, it has been shown how even low percentages of organic solvents, due to preferential solvation, can orient the photoreactivity [10, 11]. Although studies carried out in solvents characterized by different properties can provide fundamental mechanistic information, their extrapolation to environmental conditions is not straightforward. Laser flash photolysis experiments allow information on the transient species which take part in the photoreaction to be obtained, but the use of this technique in the environmental research area is still limited; the inter-

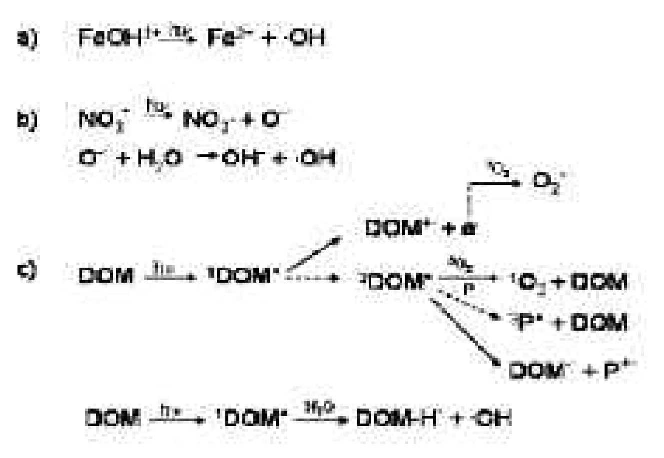


Scheme 3 - Mechanisms of photodegradation of halogenated phenylureas (from [13]) mediates and the mechanisms of reaction are often assumed on the basis of the nature of photoproducts [8]. The assessment of the effects of oxygen, rarely considered, can provide further mechanistic details, because it can take part in the reaction, for example reacting with radical intermediates, but also because it acts as a quencher towards electronically excited states. As a consequence, only for a few classes of compounds, the studies carried out have enabled a general mechanism of reaction to be proposed. Such rationalization has been made for halophenoxyacetic and halophenylura pesticides, whose photochemical behaviour has been correlated respectively with that of the halophenols and haloanilines, considered as parent chromophores [12]. The mechanisms of direct and indirect photodegradation of phenylureas have been reviewed [13]: the influence of substituents on the orientation of the reaction has been shown and the role of solvents and oxygen on reaction pathways studied. In water photohydrolysis is the main transformation process; for para-halogenated phenylureas, the intermediate formation of a carbene has been observed (Scheme 3). Developments in the mechanism of photodegradation of triazine-based pesticides have been reviewed [14].

The lack of studies carried out directly on field or in laboratory, mimicking the environmental conditions, has been underlined [15]: the main limits regard the use of mixtures of organic solvents and the widespread use of monochromatic sources with a wavelength output at 254 nm, which does not allow the extrapolation of the results to environmental conditions. Indeed, it has been demonstrated that the photochemical behaviour can depend on the excitation wavelength: in the case of organic herbicides such dependence has been shown for some sulfonylureas, as a consequence of their bichromophoric nature [10, 16], and phenoxyacetic derivatives [17].

Indirect photodegradation

Indirect phototransformations may be the dominant degradation process for those contaminants that absorb sunlight poorly or are stable against direct photolysis. This section is focused on the transformations of organic pesticides photoinduced by typical natural chromphores able to absorb sunlight, namely Fe(III) complexes, nitrate ions, dissolved organic matter (DOM). Upon excitation, they produce reactive species which can in turn degrade the majority of organic compounds; the main reactive species produced are hydrated electron, singlet molecular oxygen, hydroxyl radical, superoxide radical ion. Triplet excited states of humic substances also seem able to interact with organic compounds. In Scheme 4 some major processes that may lead to indirect photodegradation of an organic contaminant are summarized. Important aspects of research studies include the identification of the various short-lived reactive species which are produced in natural waters, the determination of their concentrations and their second-order reaction rate constants with organic compounds, in order to assess photoinduced transformation rates in the environment and the role that each reactive species plays in the transformation processes.



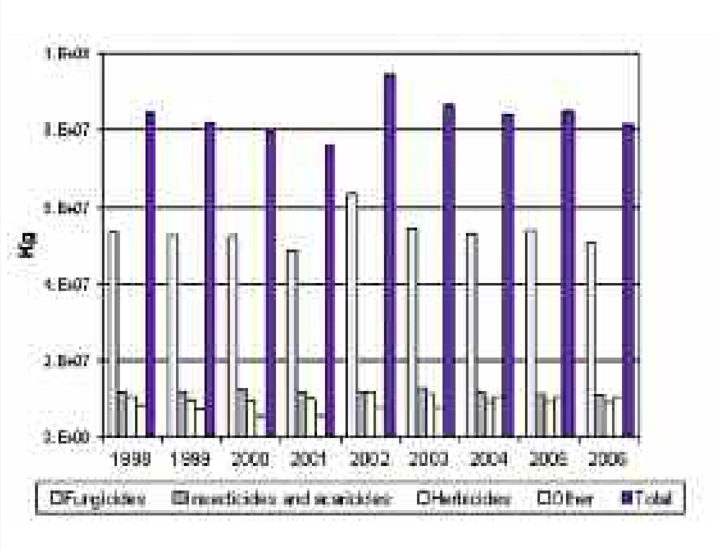
Scheme 4 - Major photochemical processes of the ferric aquacomplex (a), nitrate ions (b), DOM (c) involved in indirect photodegradation of pesticides. P=pesticide, $^1X^*$=excited singlet state of the species X, $^3X^*$=excited triplet state of the species X. The mechanism proposed for DOM is according to [29]

Fe(III)-photoinduced transformation

Inorganic ferric iron species are active chromophores: the excitation of $FeOH^{2+}$, the dominant species of aqueous ferric ions at $3<pH<5$, in the near-UV region results in the reduction of metal centre to Fe(II) and generation of hydroxyl radicals (*a* in Scheme 4). The Fe(III)-induced phototransformations of pollutants are widely used for wastewater treatment (photo-Fenton process), but a deepening of this research area is beyond the scope of this review, focused on phototransformations in natural environmental conditions. The ˙OH radicals photochemically generated by $FeOH^{2+}$ have been shown to be effective oxidants for a wide range of organic contaminants, including the herbicides diuron [18] and asulam [19]. The degradation products are produced as a result of attack on the aromatic ring and/or aliphatic chains. Whereas the photochemistry of ferric hydroxy species may be important at low pH, in the pH 6-8 range, more typical of natural waters, the concentration of these species is insufficient to induce a significant production of oxidant radicals: in these conditions, soluble complexes of Fe(III) can undergo a light-induced redox transformation, which leads to the reduction of the metal centre and degradation of the ligand or, depending upon the reaction conditions, results in production of reactive species, such as $O_2^{\cdot -}$, H_2O_2, ·OH [20], able to degrade other compounds. Iron complexes with different ligands have been investigated, both of natural and anthropic origin; groups of ligands studied in detail are carboxylic and aminocarboxylic acids.

Nitrate-photoinduced transformation

Nitrate and nitrite ions, characterized by absorption spectra showing low-energy bands centred at nearly 300 and 355 nm respectively are an important source of hydroxyl radicals in natural waters (*b* in Scheme 4), which can induce the oxidation of most organic compounds [21]. This decontamination effect can be reduced by the competition between organic matter, bicarbonate ions and organic pollutants for reaction with hydroxyl radicals. Nitrates are present in



Annual amount of pesticide active substances used in Italy (data from ISPRA "Annuario dei dati ambientali 2008")

natural waters at concentrations depending on geographic location and agricultural activities, typically in the 10^{-5}-10^{-3} M range [22]. Nitrites are present at lower concentrations than nitrates, but their photoreactivity cannot be disregarded under environmental conditions. In different aquatic environments the steady-state concentration of ·OH radicals produced upon photolysis of nitrate was estimated to be about $5x10^{-16}$ M [22]. Besides oxidation reactions, nitrite and nitrate can induce nitrations and nitrosations, whose products in some cases are mutagenic. Oxidation of pollutants by ·OH competes with the oxidation of humic substances [23] and hence the efficiency of the photoinduced degradation depends on the concentration of organic matter. The three types of reactions have been deeply studied from mechanistic and analytical points of view in the presence of phenol derivatives as substrates [24]. Few studies regard nitrate-photoinduced degradation of organic pesticides: they include the herbicides monolinuron [25] and diuron [26]; a detailed study of direct and nitrate-mediated photodegradation of atrazine has been reported [27]. Mechanistic studies and the assessment of the relative importance of nitration and nitrosation, which are expected to be minor pathways under environmental conditions, with respect to oxidation, need further work.

DOM-photoinduced transformation

UV-visible absorption spectra of DOM is characterized by a nearly exponential shape in the range 300-500 nm [28]. Despite the chemical complexity of humic substances, their photoinducing effects have been found remarkably similar: they may act as photosensitizers or precursors of reactive intermediates. Laser flash photolysis and trapping experiments have allowed the reactive species produced upon irradiation of DOM to be identified. The main photochemical processes of DOM that may lead to the degradation of an organic contaminant are reported in Scheme 4. In aerated water solutions, reactive species produced upon excitation of chromophores of DOM are hydrated electrons e^-_{aq}, superoxide anion radical $O_2^{-\cdot}$, singlet molecular oxygen $^1O_2$; other routes lead to the formation of hydroxyl radical and radical derived from DOM. Photosensitized transformations can be induced via triplet-triplet energy transfer, a process which leads to the deactivation of DOM and formation of excited triplet states of the contaminant, which may then undergo photochemical transformation. The third route of degradation is represented by a photoredeox reaction, with reduction of DOM and oxidation of the contaminant. Whereas the intermediates involved and the possible routes have been established, their relative importance is an object of discussion. Richard and Canonica [29] suggest that the role of oxygenated species produced by DOM in natural waters is negligible because of either low steady-state concentrations in the great majority of surface waters (·OH, $O_2^{-\cdot}$), or, as regards $^1O_2$, relatively low second-order reaction rate constants with many organic contaminants: most photoreactions are attributable to the reactive triplet excited states of humic matter, able to abstract electrons or hydrogen atoms from some organic molecules, or to oxidations promoted by DOM-derived radicals (radical cations, oxyl and peroxyl radicals); an electron-abstraction mechanism was proposed for phenols [30]. The degradation of phenylurea and triazine-based herbicides has been interpreted on the basis of a process involving excited triplet states of DOM [31-33]. Other studies [34] underline the role of DOM as both source and sink of ·OH radicals and assess the relative importance of nitrates and DOM as photochmical sources of ·OH.

Recently, research activity has been focused on the study of more complex systems, in order to assess the relative contributions of various photoinductors to indirect photolysis in natural waters: the role of both DOM and nitrate in promoting the photodegradation of carbaryl and alachlor have been evaluated [35, 36]. In order to investigate the synergistic or inhibitory effects that a change in the water composition can have on the photochemical fate of organic contaminants, a laboratory-based test system has been developed [37].

Photodegradation on soil surfaces

Compared to the extensive studies on photodegradation of organic chemicals in water, little is known about the heterogeneous photochemistry on soil surfaces. Photochemical reactions in heterogeneous media can differ substantially from analogous homogeneous reactions in terms of reaction rates and product distributions. The most com-

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mon experimental approach is to expose a series of thin, spiked layers to a solar simulator. However, the determination of photodegradation rate in soil is of higher complexity than it is in solution, because it is influenced by various factors, among which absorption and scattering of light by the soil itself, variable sorption of pesticides on organic and inorganic components, transport processes [38, 39]. Although developments in the determination of light intensity profiles in soil, molar absorption coefficients of adsorbed compounds and photoreaction quantum yields have been supplied [38, 40], the complexity of natural environmental surfaces makes it difficult to propose a standardised method for the quantification of the photodegradation. Several studies have been performed using either thin soil layers of different compositions and model surfaces, to assess the contribution of various soil constituents in photodegradation of organic pesticides [15, 41], but a marked lack of mechanistic studies can be underlined. Diffuse reflectance techniques are a powerful tool for the understanding of mechanistic aspects and, combined with the analytical characterization of the products, may lead to new information on photochemical processes on surfaces [42].

Concluding remarks

Light-induced transformations are important degradation pathways for organic pesticides in the environment. Studies on direct photodegradation have been focused mainly on kinetic and analytical aspects, whereas knowledge of the relevant mechanisms under environmental conditions requires further research work. In indirect photoreactions the important role played by dissolved organic matter, nitrate ions and compounds of Fe(III) has been reported; further detailed studies would be required to assess the relative importance of the various photoactive species and their role under environmental conditions.

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RIASSUNTO

Fotodegradazione dei pesticidi organici nell'ambiente

Le reazioni indotte dall'assorbimento di luce contribuiscono alla degradazione di molti composti chimici nell'ambiente. Si riporta una revisione critica dell'attuale attività di ricerca inerente i processi di fotodegradazione diretta e indiretta di pesticidi organici nell'ambiente acquoso e sul suolo.