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Q1 Review

2 Review of the photo-induced toxicity of environmental contaminants

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A B S T R A C T

Solar radiation is a vital component of ecosystem function. However, sunlight can also interact with certain xenobiotic compounds in a phenomenon known as photo-induced, photo-enhanced, photo-activated, or photo-toxicity. This phenomenon broadly refers to an interaction between a chemical and sunlight resulting in increased toxicity. Because most aquatic ecosystems receive some amount of sunlight, co-exposure to xenobiotic chemicals and solar radiation is likely to occur in the environment, and photo-induced toxicity may be an important factor impacting aquatic ecosystems. However, photo-induced toxicity is not likely to be relevant in all aquatic systems or exposure scenarios due to variation in important ecological factors as well as physiological adaptations of the species that reside there. Here, we provide an updated review of the state of the science of photo-induced toxicity in aquatic ecosystems.

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49 Contents

43	1. Introduction	0
44	2. Mechanisms of photo-induced toxicity	0
45	2.1. Photosensitization	0
46	2.2. Modified photoproducts	0
47	3. Specific phototoxic compounds	0
48	3.1. Polycyclic aromatic hydrocarbons	0
49	3.2. Pesticides	0
50	3.3. Metals	0
51	3.4. Emerging contaminants	0
52	4. Modeling photo-induced toxicity	0
53	5. Ecological considerations	0
54	6. Conclusions	0
55	Funding sources	0
56	References	0

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Q3 1. Introduction

59 Rarely are organisms exposed to one stressor in their environment.
60 More commonly, populations of organisms are exposed to a complex
61 mixture of toxicants and stressors, both natural and anthropogenic. In

recent years, greater emphasis has been placed on evaluating the effects
of multiple stressors within aquatic ecosystems (De Zwart et al., 2006;
Gevertz et al., 2012; Newman et al., 2007; Sandland and Carmosini,
2006). The idea of multiple stressors includes not only mixtures of
chemical contaminants but also “mixtures” of non-chemical stressors.
These other stressors include low dissolved oxygen, dietary deficiencies,
and predation stress. It has been demonstrated that these non-chemical
stressors can interact additively, or in some cases synergistically, with
chemical stressors and have impacts on individuals, populations, and
communities (De Zwart et al., 2006; Gevertz and Oris, 2014; Gevertz

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et al., 2012; Heugens et al., 2006; Pelletier et al., 2006; Perrett et al., 2006; Sandland and Carosini, 2006).

Solar radiation, an important component of most ecosystems, can also play a role as an ecological stressor. Exposure to specific wavebands of sunlight, such as ultraviolet radiation, can result in increased oxidative stress and damage to biological macromolecules (Babu et al., 2003; Buma et al., 2006; Casati and Walbot, 2004; Haeder and Sinha, 2005; Obermuller et al., 2005; Olson et al., 2006). Sunlight can also interact with certain xenobiotic compounds in a phenomenon known as photo-induced, photo-enhanced, photo-activated, or photo-toxicity (Arfsten et al., 1996; Cho et al., 2003; Diamond, 2003; Diamond et al., 2003, 2006; Oris et al., 1990; Weinstein, 2002, 2003; Weinstein and Diamond, 2006; Weinstein et al., 1997). Photo-induced toxicity broadly refers to an interaction between a chemical and sunlight resulting in increased toxicity. Because most aquatic ecosystems receive some amount of sunlight, co-exposure to xenobiotic chemicals and solar radiation is likely to occur in the environment, and photo-induced toxicity may be an important factor impacting aquatic ecosystems. However, photo-induced toxicity is not likely to be relevant in all aquatic systems or exposure scenarios due to variation in important ecological factors. Here, we present an updated evaluation of the state of the science incorporating significant research done since previous reviews (Arfsten et al., 1996; Diamond, 2003).

2. Mechanisms of photo-induced toxicity

The general mechanism of photo-induced toxicity involves the absorption of specific wavelengths of solar radiation by a chemical compound (Diamond, 2003) and follows the laws of photochemistry. The Grotthus-Draper law of photochemistry states that energy from light must be absorbed by a compound in order for a reaction to occur. The Stark-Einstein law states that the absorbed light is quantized. In other words, only specific energies of light (i.e., wavelengths) will be absorbed by a compound based on the exact energy differences between the outer shell electrons' ground state and excited state orbitals. The energy released as excited state electrons return to ground state follows a variety of pathways. Excited state energy can be released as light (fluorescence or phosphorescence), as heat, to other molecules such as oxygen or biomolecules, by reorganizing or breaking covalent bonds, or by a combination of these pathways. Energy passed to other molecules or which results in the creation of reactive chemicals may lead to toxic reactions in organisms.

Even though a majority of compounds will absorb and release energy from defined wavelength ranges, only a handful of chemical classes act as phototoxic compounds in the aquatic environment. Typically, only compounds that have absorption spectra in the near UV (285–400 nm) or visible (400–700 nm) range will act as phototoxicants because these wavelengths are present in aquatic systems. These compounds often have multiple and conjugated double covalent bonds, large electrophilic constituents, or heteroatoms with non-bonding electrons. Examples of phototoxic chemicals include polycyclic aromatic hydrocarbons (PAHs) such as anthracene, organic pesticides such as carbaryl, metalloids such as arsenic, pharmaceuticals such as tetracycline, and nanoparticles such as titanium dioxide.

2.1. Photosensitization

In aquatic systems, photosensitization is generally thought to be the most important phototoxic mechanism (Arfsten et al., 1996; Diamond, 2003). Photosensitization reactions can come in two forms; Type I and Type II (Foote, 1991). Type I photosensitization occurs when the energy given off from the excited state electrons is passed on directly to a cellular constituent or molecule such as cell membrane lipids. Type II photosensitization occurs when that energy is passed on directly to molecular oxygen (O₂). Both of these reactions can result in increased levels of oxidative stress through the formation of reactive oxygen species (ROS)

and free radicals. These free radicals and ROS can interact with cellular constituents including lipids. Free radicals are able to start lipid peroxidation chain reactions in which lipid peroxy radicals abstract hydrogens from lipid molecules eventually resulting in the formation of other lipid peroxy radicals.

Choi and Oris demonstrated that coexposure to anthracene (a model phototoxic PAH) and ultraviolet radiation resulted in increased signs of oxidative stress in sunfish liver microsomes (Choi and Oris, 2000b). These included increased superoxide anion production and lipid peroxidation (Choi and Oris, 2000b). The authors also demonstrated that anthracene photo-induced toxicity could be ameliorated in the topminnow cell line (PLHC-1) with antioxidant pretreatment (Choi and Oris, 2000a). These studies provide strong evidence that oxidative stress and reactive oxygen species play a significant role in the mechanism of phototoxicity. In vivo studies demonstrate that this oxidative stress may ultimately affect the organism's ability to osmoregulate and transport oxygen across gill membranes (McCloskey and Oris, 1993; Weinstein et al., 1997).

2.2. Modified photoproducts

It is well-known that exposure to solar radiation can alter the chemical structure of contaminants in aquatic systems. Photolysis is, in fact, considered a major pathway of degradation for a number of chemicals. Some research has suggested that the products of reactions between solar radiation and parent compounds (photoproducts) may exert greater toxicity than the parent compound (Arfsten et al., 1996; Lampi et al., 2006). These studies have typically focused on polycyclic aromatic hydrocarbons (PAHs) and involve the irradiation of stock solutions prior to exposures with biota. These modified PAHs have been shown to have effects on invertebrates, plants, and bacteria (El-Alawi et al., 2002; Huang et al., 1997a; Lampi et al., 2006; Marwood et al., 2003).

3. Specific phototoxic compounds

A wide range of chemical compounds have been shown to exhibit photo-induced toxicity from natural products to pesticides to fossil fuel derivatives. This can occur either through photosensitization or photomodification reactions (Fig. 1). Certain plants have evolved the use of phototoxic compounds as a defense mechanism against predators (Diamond, 2003). Dinitrotoluenes (Davenport et al., 1994), pharmaceuticals (Pandey et al., 2002), pesticides (Zaga et al., 1998), and PAHs (Arfsten et al., 1996) are all compounds which have been shown to have phototoxic properties.

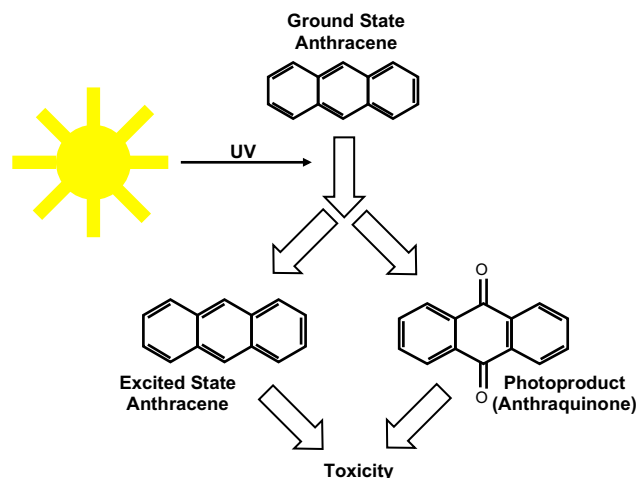


Fig. 1. Mechanism of photo-induced toxicity of the polycyclic aromatic hydrocarbon anthracene.

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