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Water quality parameters controlling the photodegradation of two herbicides in surface waters of the Columbia Basin, Washington

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HIGHLIGHTS

- Surface water samples were collected from four sites over the irrigation season.
- Nitrate-nitrogen, dissolved organic carbon (DOC), and suspended solids were measured.
- Atrazine and 2,4-D photolysis rates were correlated with water quality parameters.
- Nitrate-nitrogen was the primary predictor of photolysis for both atrazine and 2,4-D.
- High suspended solids concentrations also inhibited photolysis of atrazine and 2,4-D.

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ABSTRACT

The water quality parameters nitrate-nitrogen, dissolved organic carbon, and suspended solids were correlated with photodegradation rates of the herbicides atrazine and 2,4-D in samples collected from four sites in the Columbia River Basin, Washington, USA. Surface water samples were collected in May, July, and October 2010 and analyzed for the water quality parameters. Photolysis rates for the two herbicides in the surface water samples were then evaluated under a xenon arc lamp. Photolysis rates of atrazine and 2,4-D were similar with rate constants averaging 0.025 h^{-1} for atrazine and 0.039 h^{-1} for 2,4-D. Based on multiple regression analysis, nitrate-nitrogen was the primary predictor of photolysis for both atrazine and 2,4-D, with dissolved organic carbon also a predictor for some sites. However, at sites where suspended solids concentrations were elevated, photolysis rates of the two herbicides were controlled by the suspended solids concentration. The results of this research provide a basis for evaluating and predicting herbicide photolysis rates in shallow surface waters.

1. Introduction

Herbicides are applied to crop lands in every agricultural region in the United States. Although the benefits of their use are undisputed, runoff of these xenobiotics into surface water can result in threats to public health and the environment (Krieger, 2010). Herbicide fate in the environment depends on the rate of application, the physicochemical properties of the herbicide, transport pathways, and transformation processes in soil and water (Payraudeau and Gregoire, 2012). Herbicide transformation processes include abiotic oxidation and reduction, hydrolysis, biodegradation, and photolysis (Schnoor, 1991). Biodegradation is the primary herbicide transformation process in soils, and photolysis is the primary transformation pathway in surface waters (Goncalves et al., 2006).

Photodegradation of xenobiotics in surface waters may proceed by direct or indirect pathways. In direct photolysis, the xenobiotic itself acts as a chromophore; it absorbs light energy which then disrupts chemical bonds resulting in its degradation. Indirect photolysis occurs when another compound acts as a chromophore and then transfers energy to the xenobiotic, resulting in its decomposition (Pinna and Pusino, 2011). Common indirect photolysis chromophores include nitrate, minerals, and dissolved natural organic matter (NOM) (Boule et al., 2010).

Nitrate, a highly mobile anion that is ubiquitous in surface waters as a result of fertilizer application, absorbs the near-uv light of sunlight to generate reactive oxygen species. Nitrate-induced photolysis is initiated by the absorbance of sunlight at a maximum of 313 nm, resulting in the generation of the strong oxidant hydroxyl radical ($OH^{\cdot}$) (Zepp et al., 1992):

$$NO_3^- + H_2O + h\nu \rightarrow NO_2^{\cdot} + OH^{\cdot} + OH \tag{1}$$

$$NO_2^{\cdot} + OH^{\cdot} + OH^- \rightarrow NO_2^- + {}^{\cdot}O^{\cdot} \tag{2}$$

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$$NO_2^- + H_2O + h\nu \rightarrow NO^{\cdot} + OH^{\cdot} + OH^- \quad (3)$$

Although nitrate-induced photolysis is a dominant pathway for generating hydroxyl radical in surface waters, dissolved organic matter (DOM) is often a more important light-absorbing material (Page et al., 2011). Common components of DOM that function as sensitizers include humic and fulvic acids (i.e., aquatic humus) and riboflavin (Jacobs et al., 2011). Aquatic humus absorbs a significant amount of light between 290 and 450 nm, and therefore has a significant role as a photosensitizer in natural waters. Several reactive oxygen species can be formed when DOM is excited by sunlight (Dalrymple et al., 2010). One mechanism is the excitation of DOM by a photon to its triplet state. When the DOM triplet state returns to ground state, the energy can be transferred to molecular oxygen to form singlet molecular oxygen:

$$^3DOM + O_2 \rightarrow DOM + {}^1O_2 \quad (4)$$

In another proposed mechanism the excited DOM molecule releases an aqueous electron, which is then scavenged by molecular oxygen to generate superoxide radical anion ($O_2^{\cdot-}$) (Larson and Weber, 1994):

$$^*DOM \rightarrow DOM + e^-_{aq} \quad (5)$$

$$e^-_{aq} + O_2 \rightarrow O_2^- \quad (6)$$

Superoxide may then dismutate to hydrogen peroxide (H_2O_2), which can then decompose to hydroxyl radical through reactions catalyzed by transition metals or metal oxide minerals:

$$O_2^- + 2H^+ \xrightarrow{SOD} H_2O_2 \quad (7)$$

$$H_2O_2 \xrightarrow{Me^{n+}, Me_xO_y} OH^{\cdot} + OH^- \quad (8)$$

Hydroxyl radical has the potential to oxidize a wide range of xenobiotics. DOM-sensitized photolysis has been shown to degrade a number of xenobiotics including trifluralin (Dimou et al., 2004), atrazine (Prosen and Zupancic-Krajl, 2005), imazaquin and iprodione (Garbin et al., 2007), alloxydim (Sevilla-Moran et al., 2008), and methyl parathion (Manzanilla-Cano et al., 2008).

The Columbia River Basin of eastern Washington State, USA, is an agricultural area in which alfalfa, apples, and wheat represent the largest crop acreages. Atrazine, bentazon, diuron, and 2,4-dichlorophenoxyacetic acid (2,4-D) are the most frequently detected herbicides in surface waters in the Columbia Basin as well as throughout the entire US (USGS, 2006). These herbicides have relatively high solubilities in water; therefore, they are potentially transported into surface waters and ground waters (Watts, 1998).

Nitrate and DOM are chromophores that have the potential to promote herbicide photodegradation in surface waters, while suspended solids may inhibit photodegradation by blocking light penetration into surface waters. The objective of this research was to elucidate which of three water quality parameters, nitrate-nitrogen concentration, dissolved organic carbon concentration, and suspended solids concentration, control the photolysis rate of two of the most commonly used herbicides in the Columbia Basin of Washington State, atrazine and 2,4-D. Because surface water characteristics and herbicide fate and transport are affected by seasonality (USGS, 2006), seasonal effects on the photodegradation of herbicides were also evaluated.

2. Material and methods

2.1. Materials

Borosilicate glass sampling bottles (1 L) and 0.45 μm membrane filters were purchased from VWR Scientific (West Chester, PA, USA). Atrazine, 2,4-D, hexane, boron trifluoride/methanol (12/88%, m/m), phthalic acid, and acetonitrile were purchased from Sigma Aldrich (Milwaukee, WI, USA). Double-deionized water (>18 MΩ cm) was produced using a Barnstead Nanopure II ultrapure system.

2.2. Sample collection and characterization

Surface water samples were collected in 2010 from sites in four drainages of the Columbia Basin, Washington State, USA: Crab Creek, Lind Coulee, Red Rock Coulee, and Sand Hollow (Fig. 1). Geographical coordinates of the sampling sites were: Crab Creek, latitude 46°49′48″, longitude 119°49′48″; Lind Coulee, latitude 47°00′37″, longitude 119°08′10″; Red Rock Coulee, latitude 46°51′20″, longitude 119°35′48″; Sand Hollow, longitude 46°55′46″, latitude 119°57′01″. Sampling sites have been established in these drainages by the US Geological Survey to examine the occurrence, distribution, and transport of pesticides in agricultural irrigation return flows (USGS, 2006). These surface-water drainages from irrigated lands lead to wasteway returns that create irrigation-return flows to major streams and rivers. More than 95% of the cropland in Crab Creek, Red Rock Coulee, and Sand Hollow drainage basins is irrigated, whereas only 30% of the cropland in Lind Coulee is irrigated. The Crab Creek basin drains 767 km^2, and its site near Beverly is directly affected by ground water seepage from Potholes Reservoir (USGS, 2006). The largest of the four drainage basins sampled, Lind Coulee, covers 1839 km^2; it flows through the town of Lind and empties into Potholes Reservoir. Red Rock Coulee is the smallest of the four drainage basins, draining about 49 km^2 of land from the eastern boundary of Grant County to Crab Creek. Sand Hollow covers 155 km^2 from the western flanks of Royal Slope to the Columbia River.

To examine a possible seasonal effect, samples were collected in May, July, and October, 2010; i.e., at the beginning, middle, and end of the irrigation season. Five samples from each site were collected directly into 1-L borosilicate glass bottles fitted with PTFE-lined caps, shipped on ice to Washington State University, and stored at <4 °C.

Surface water samples were composited before being characterized for nitrate-nitrogen, dissolved organic carbon, and suspended solids concentrations. Subsamples for the analysis of nitrate-nitrogen and dissolved organic carbon were passed through a 0.45 μm filter. Field blanks and equipment blanks were analyzed to control for possible contamination. All analyses were conducted in triplicate.

2.3. Photodegradation studies

Unfiltered surface waters samples were spiked with 10 $mg\ L^{-1}$ of atrazine or 2,4-D. Irradiation of the samples was performed in quartz tubes (outside diameter = 1.3 cm, inside diameter = 1.1 cm, volume = 10 mL) in a Suntest CPS chamber (Heraeus, Germany) equipped with a xenon arc lamp and a filter restricting transmission of light below 290 nm. The emitted wavelengths ranged from 290 nm to 800 nm, and irradiation was set at 765 $W\ m^{-2}$ to simulate sun irradiance. The temperature within the reactor was maintained at 30 ± 2 °C by using a fan. Parallel dark control samples covered with aluminum foil were also placed in the Suntest reactor to account for other transformation processes such as volatilization and hydrolysis. Photodegradation of atrazine and 2,4-D was measured as a function of time by collecting aliquots from a triplicate set of reactors. The aqueous aliquots were shake-extracted with hexane and analyzed for atrazine and 2,4-D by gas chromatography (GC).