Photolytic degradation of quinalphos in natural waters and on soil matrices under simulated solar irradiation

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Abstract

The photochemical persistence of quinalphos, one of the most widely used organophosphorous insecticides, was investigated in a variety of environmental matrices such as natural waters and soils of different composition. Simulated solar irradiation was obtained using a xenon arc lamp (Suntest CPS+ apparatus) giving an irradiation intensity of 750 W m$^{-2}$ equivalent to a light dose per hour of irradiation of 2700 kJ m$^{-2}$. The phototransformation rates were determined using solid-phase microextraction (SPME) and ultrasonic extraction (USE) coupled to GC-FTD, while the identification of photoproducts was carried out by GC–MS.

In water samples, the degradation kinetics followed a pseudo-first-order reaction and photolysis half-lives ranged between 11.6 and 19.0 h depending on the constitution of the irradiated media. Dissolved organic matter (DOM) has a predominant retarding effect, while nitrate ions accelerated the photodegradation kinetics. In soil samples, the degradation kinetics was monitored on 1 mm soil layer prepared on glass TLC plates. The kinetic behaviour of quinalphos was complex and characterized by a double step photoreaction, fast in the first 4 h of irradiation followed by a slow degradation rate up to 64 h. The photolysis half-life of quinalphos was shorter in sandy soil compared to the rest of the soil samples, varying between 16.9 and 47.5 h, and showing a strong dependence on the composition of the irradiated media. Among the transformation products formed mainly through photohydrolysis and photoisomerization processes, some photoproduct structures were proposed according to their mass spectral information.

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1. Introduction

Organophosphorous pesticides (OPPs) are generally seen as safe chemicals for use on crops and animals due to their relatively fast degradation rates. However, they are also by far the most toxic to humans of all pesticides (Ragnarsdottir, 2000). Because of the magnitude of their application, often as replacement of the organochlorine pesticides, they are most frequently detected in the environment. OPPs have relatively high solubilities in water (quinalphos –17.8 mg l$^{-1}$, at 22–23 °C (Tomlin, 1999)), thus they are transported readily through soils and into groundwaters or surface waters (Ragnarsdottir, 2000). Actual dissipation rates may be dependent on a number of natural water conditions including pH, salinity, dissolved organic matter (DOM) and metals (Liu et al., 2001). In soil, many environmental factors may affect dissipation rates including soil type, moisture, organic matter, microbial activity, sunlight intensity, amenability to aeration as well as weather conditions (Hebert and Miller, 1990; Hultgren et al., 2002; Das et al., 2005). Pesticides may follow a range of dissipation pathways among which volatilization, hydrolysis, photolysis and biodegradation are the main processes. For some pesticides photolysis may be dominant on dry, sunlight-exposed surfaces, while other dissipation