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Gas-phase degradation of the herbicide ethalfluralin under atmospheric conditions

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HIGHLIGHTS

- The gas phase atmospheric degradation of ethalfluralin was investigated at EUPHORE.
- Photolysis carried out under ambient conditions and natural sunlight irradiations.
- First experimental value for the reaction of ethalfluralin with sunlight.
- First experimental value for the reaction of ethalfluralin with OH radicals.
- The atmospheric lifetime of ethalfluralin is 12 min.

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ABSTRACT

The gas-phase degradation of ethalfluralin, *N*-ethyl-α,α,α-trifluoro-*N*-(2-methylallyl)-2,6-dinitro-*p*-toluidine, a widely used herbicide, was investigated under atmospheric conditions at the large outdoor European simulation chamber (EUPHORE) in Valencia, Spain. The photolysis of ethalfluralin was investigated under solar radiation and the mean photolysis rate coefficient was determined: $J(\text{ethalfluralin}) = (1.3 \pm 0.2) \times 10^{-3}\ s^{-1}$ ($J_{NO2} = 8 \times 10^{-3}\ s^{-1}$). The rate coefficients for the reactions of hydroxyl radicals and ozone with ethalfluralin in the dark were also measured under atmospheric conditions using the relative rate and the absolute rate technique, respectively. The rate coefficients values for the reactions of $k_{OH}(\text{ethalfluralin}) = (3.5 \pm 0.9) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$, and $k_{O3}(\text{ethalfluralin}) = (1.6 \pm 0.4) \times 10^{-17}\ cm^3\ molecule^{-1}\ s^{-1}$ were determined at 300 ± 5 K and atmospheric pressure. The results show that removal of ethalfluralin from the atmosphere by reactions with OH radicals ($\tau \sim 4$ h) or ozone ($\tau \sim 25$ h) is slow compared to loss by photolysis. The available kinetic data suggest that the gas-phase tropospheric degradation of ethalfluralin will be controlled mainly by photolysis and provide an estimate for the tropospheric lifetime of approximately 12 min. The atmospheric implications of using ethalfluralin as a herbicide are discussed.

1. Introduction

Chemical pesticides have been increasingly employed worldwide in crop protection over the last two decades, which has led to contaminated soil, water and atmosphere in treated and remote areas. Pesticides are partitioned among soil, water and the atmosphere following application, and concern has been expressed for the possible effects of pesticides and their degradation products on human health and on the environment (Konradsen et al., 2003). Knowledge of the fate of pesticides and their degradation products following their use is required to assess the potential environmental impact of pesticides.

Pesticides can be emitted into the atmosphere as a result of drift during spraying operations, volatilisation from ground or leaf surfaces and wind erosion (Yusa et al., 2009; Espallardo et al., 2012). The amount of a pesticide entering the atmosphere depends on its physical properties and the method of application. The atmosphere provides an important transport medium and reservoir for pesticides and their residues (Wania and Mackay, 1996). In the atmosphere, pesticides are distributed among gas, aqueous and particle phases in accordance with their physical properties and atmospheric conditions (Tsai and Cohen, 1991). A pesticide is expected to be removed from the atmosphere by wet and dry deposition (Bidlemann, 1988), and by chemical degradation (Atkinson

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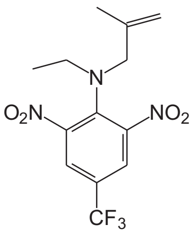
et al., 1999). The sum of the rates of all these processes determines the atmospheric persistence of a pesticide.

Dinitroanilines are selective herbicides used for the pre-emergent control of a wide spectrum of annual grasses and broad-leafed weeds in a wide variety of agro-economically important crops. Ethalfluralin has been employed extensively for the protection of crops such as cotton, maize, soya beans, peppers, tomatoes, lentils, peanuts and sunflowers.

Ethalfluraline, (*N*-ethyl-α,α,α-trifluoro-*N*-(2-methylallyl)-2,6-dinitro-*p*-toluidine),



is often available as an emulsifiable concentrate that is mixed with water and used as a spray. It does not hydrolyze, but degrades in surface water due to photolysis by solar radiation. It is generally applied by surface spraying after planting, and prior to crop or weed emergence. Ethalfluralin has been employed in many countries for over 30 years, including the European Union and the United States. Ethalfluralin is supported by Dow AgroSciences and approved for use in several countries, where it remains a valued product by the agricultural community. In the European Union, as lead registrant, Dow AgroSciences decided not to pursue the continued registration of this substance in 2010 for strategic reasons. However, the worldwide use of ethalfluralin is unlikely to significantly decrease in the immediate future, and is increasingly being used in developing countries.

Ethalfluralin, classified as a Semi-Volatile Organic Compound (SVOC), has a vapour pressure of 1.2×10^{-2} Pa (8.9×10^{-5} mm of Hg) at 25 °C, and a Henry's law constant of 18 Pa m^3 mol^{-1}, indicating that it has a tendency to volatilise from aqueous solutions. Thus, ethalfluralin is sufficiently volatile and may be emitted into the atmosphere, unless it is covered or incorporated into soil. Monitoring programmes in Europe and Canada at remote, rural and urban sites have detected ethalfluralin levels in air samples within the 0–41 ng m^{-3} range (Waite et al., 2005; Yao et al., 2008; Yusa et al., 2009). These concentrations are referred to as the sum of the gas and particle phases.

This work is a study of the atmospheric degradation of ethalfluralin. Chemical degradation of volatile organic compounds in the atmosphere may be initiated by photolysis, and by reaction with hydroxyl and nitrate radicals or ozone (Atkinson and Arey, 2003). The experiments were performed at the large outdoor European Photoreactor (EUPHORE). This simulation chamber enables reactions to be carried out at realistic atmospheric concentrations, and at solar wavelengths and intensities by following procedures similar to those previously employed in this laboratory to investigate the atmospheric fate of a number of pesticides; i.e., trifluraline, chlorpyriphos-methyl, diazinon and propachlor (Le Person et al., 2007; Muñoz et al., 2011a,b, 2012). The data obtained in this study provide information on the atmospheric lifetime of ethalfluralin with respect to photolysis, and for the reaction with OH radicals and O_3. Possible ethalfluralin degradation mechanisms under atmospheric conditions are discussed in terms of the impact on the environment of ethalfluralin emissions into the atmosphere.

2. Experimental section

Ethalfluralin photolysis experiments were performed under sunlight conditions at the outdoor European Photoreactor (EUPHORE) in Valencia, Spain (longitude = −0.5°, latitude = 39.5° N). The rate coefficients for the reaction of OH radicals and ozone with ethalfluralin were also determined in the chamber in the dark. Technical information about the facility has been previously reported in the literature (Muñoz et al., 2011a and references therein), and only a brief description of the system is provided in the Supporting Information.

Photolysis of ethalfluralin (99.5%, Chem Service) was carried out in the presence of cyclohexane (99.7%, Scharlau). Cyclohexane and ethalfluralin were added to the chamber *via* a stream of purified air. Given its relatively low vapour pressure, ethalfluralin was gently heated to accelerate its introduction into the chamber. The absolute rate study on the reaction of ethalfluralin with O_3, which was produced by passing oxygen through an ozone generator and transferring directly into the chamber, was performed with similar concentrations of ozone and ethalfluralin. Cyclohexane was added to the system as a scavenger of OH. It is one of the most widely used OH radical scavengers in the gas phase at EUPHORE and other chambers (i.e.: Feigenbrugel et al., 2006; O'Connor et al., 2006; Muñoz et al., 2012). Relative rate studies on the reaction of OH radicals with ethalfluralin were conducted using 1,3,5-trimethyl benzene (TMB), (99%, Fluka) as the reference compound. Hydroxyl radicals were generated in the dark from the reaction of 2,3-dimethyl-2-butene with O_3.

Reactants were allowed to mix for at least 30 min before starting any of the experiments. The dilution rate of the chamber was determined by adding an inert tracer gas SF_6 (99%, Abelló-Linde) to the reaction mixtures at the beginning of the experiments. The decay of SF_6 was continuously monitored by FTIR spectroscopy.

3. Results and discussion

3.1. Reaction of ethalfluralin with ozone

The second-order rate coefficient for the reaction of O_3 with ethalfluralin k_{O3}(ethalfluralin) was determined in an experiment carried out with similar concentrations of the reactants by simultaneously monitoring loss of ozone and ethalfluralin.

$$O_3 + \text{Ethalfluralin} \rightarrow \text{Products } k_{O3}(\text{ethalfluralin}) \quad (1)$$

$$O_3 + \text{Wall} \rightarrow \text{Wall loss } k_{wall}(O_3) \quad (2)$$

$$O_3 \rightarrow \text{Dilution } k_{\text{dil}} \quad (3)$$

$$\text{Ethalfluralin} + \text{Wall} \rightarrow \text{Wall loss } k_{\text{wall}}(\text{ethalfluralin}) \quad (4)$$

$$\text{Ethalfluralin} \rightarrow \text{Dilution } k_{\text{dil}} \quad (5)$$

Loss of SF_6 from the chamber was used to measure the leak rate coefficient, k_{dil}, during the experiment.

$$SF_6 \rightarrow \text{Dilution } k_{\text{dil}} \quad (6)$$

The temporal concentration–time profile for SF_6 is given by:

$$\ln([SF_6]_o/[SF_6]_t) = k_{\text{dil}}t \quad (I)$$

where $[SF_6]_o$ and $[SF_6]_t$ are the concentrations of SF_6 initially and at time t, respectively.

The dilution rate coefficient k_{dil} during the ozonolysis experiment was $(5.8 \pm 0.2) \times 10^{-6}$ s^{-1}, where the quoted error corresponds to 2σ obtained from the least-squares fit of the SF_6 decay