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Near-UV molar absorptivities of alachlor, mecroprop-p, pendimethalin, propanil and trifluralin in methanol

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Abstract

An experimental set-up consisting of two parallel absorption cells coupled to a CCD detector was used to determine absolute values of molar absorptivity coefficients ε of five herbicides (alachlor, mecoprop-p, pendimethalin, propanil and trifluralin) in methanol. The absorption spectra were measured using a deuterium lamp at room temperature (298 ± 2 K) over the wavelength range 240–340 nm, except for pendimethalin and trifluralin where the wavelength range was extended to 240–550 nm.

Absorbances were also measured at 253.7 nm using an Hg-lamp in different concentrations range depending on the studied compound. Except for mecoprop-p where absorbances were too low at this wavelength, the absolute values of molar absorptivity coefficients at 253.7 nm were determined according to the Beer–Lambert's law: $\varepsilon = 381 \pm 28$ for alachlor, $\varepsilon = 11{,}240 \pm 1030$ for pendimethalin, $\varepsilon = 22{,}220 \pm 1850$ for propanil and $\varepsilon = 5720 \pm 410$ for trifluralin (in units of $M^{-1}\,cm^{-1}$). The quoted errors correspond to 2σ obtained from the least square fit analysis and the estimated systematic error of 5% due to the uncertainties in aqueous concentrations. For all the studied compounds, the absorbances measured were lower than two and did not exhibit any deviation from the Beer–Lambert's law.
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Keywords: Pesticide; Herbicide; UV spectrum; Molar absorptivity; Alachlor; Mecoprop-p; Pendimethanlin; Propanil; Trifluralin

1. Introduction

The amount of pesticides routinely applied, mainly for agricultural uses, has dramatically increased in recent years and consequently, there are serious concerns about the increasing risks to human health.

This study has been focused on five herbicides belonging to various chemical families, namely alachlor (chloroacetanilide), mecoprop-p (aryloxyacid), pendimethalin (dinitroaniline), propanil (amide) and trifluralin (dinitroaniline) for which the absolute molar absorptivity has been determined over the wavelength range 240–340 or 240–550 nm.

Propanil is mainly used on the cultures of rice whereas mecoprop-p is a commonly used lawn herbicide. Chloroacetanilides such as alachlor are widely used herbicides, applied as pre-planting, pre-emergent or early post-emergent treatment to control annual grass weeds and broadleaf weeds in soybeans, corn, sorghum, sweet corns and dry beans [1]. Both trifluralin and pendimethalin are dinitroaniline herbicides. Trifluralin is used primarily as an herbicide on grass, to control broadleaf weeds and on some crops (fruits and vegetables), flowers and shrubs. For example, trifluralin is used on soybeans and cotton. Pendimethalin is used primarily as an herbicide to destroy or prevent the growth of certain plants like weeds. It is also used on crops and residential lawns and ornamentals. Estimated U.S. annual uses of alachlor, pendimethalin, propanil and trifluralin in 1997 were 6.8×10^6, 12.3×10^6, 3.6×10^6 and 10.0×10^6 kg, respectively [1].

Alachlor, propanil, mecoprop-p are slightly toxic herbicides as illustrated by their rat oral LD50 values (in units of mg/kg): 930–1350 for alachlor, 930–1210 for mecoprop-p and 1080–2500 for propanil [2]. Pendimethalin is slightly to practically non-toxic by ingestion, with reported oral LD50 values of 1050 mg/kg to greater than 5000 mg/kg in rats while pure trifluralin is practically non-toxic to test animals by oral, dermal, or inhalation routes of exposure. The oral LD50 for technical trifluralin in rats is greater than 10,000 mg/kg. Except mecoprop-p that may be mutagenic at very high

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doses, all the studied herbicides have no mutagenic activity. If propanil and pendimethalin are not carcinogenic, the carcinogenic effects for the three others herbicides are uncertain [2].

Once in the environment, pesticides can contaminate surface water and groundwater depending on their solubilities while the main input mechanisms of pesticides in the atmosphere are dispersion during spraying operations, volatilisation from ground or leaf surfaces and wind erosion [3]. Their resulting atmospheric concentrations are usually relatively low and vary according to the seasons [3]. For example, the maximum concentrations recorded in France in the region centre in 2002 were 17.8, 5.7 and 11.4 ng m^{-3} for alachlor, pendimethalin and trifluralin, respectively [4].

Direct photolysis is a possible pathway for the elimination of pesticides in the environment. The photodissociation rate constants associated to these components depend either on their absorption cross sections $\sigma(\lambda)$ for the molecule in the gas-phase or on their molar absorptivity coefficients $\varepsilon(\lambda)$ for the molecule in the aqueous phase, on the primary quantum yield $\phi(\lambda)$ for photolysis and on the actinic flux of solar radiation $J(\lambda)$. Due to the low vapor pressures of pesticides, the direct measurements of their absorption cross sections in the gas-phase cannot be performed using a classical absorbance cell [5,6].

Besides, the pesticides are generally poorly soluble in water so that direct measurements of ε using a classical pathlength of 1 cm is rather limited, except if they exhibit high absorbance. A set-up based on a long pathlength allows the determination of the molar absorptivity coefficients for species with relative low solubility in water [7,8]. In the case of very low soluble species in water like the studied herbicides, absorption measurements can then be performed in an adequate solvent.

In this work, the absolute values of molar absorptivity coefficients ε of alachlor, mecoprop-p, pendimethalin, propanil and trifluralin have been measured in methanol at room temperature (298 ± 2 K), over a wavelength range of either 240–340 nm or 240–550 nm using an absorbance cell coupled to a CCD detector. The chemical formulas of the five studied pesticides are given in Fig. 1. Alachlor measurements performed in methanol in this work were compared to those obtained in water in our previous study [7] in order to validate our new experimental set-up and ensure that results did not depend on the solvent. To our knowl-

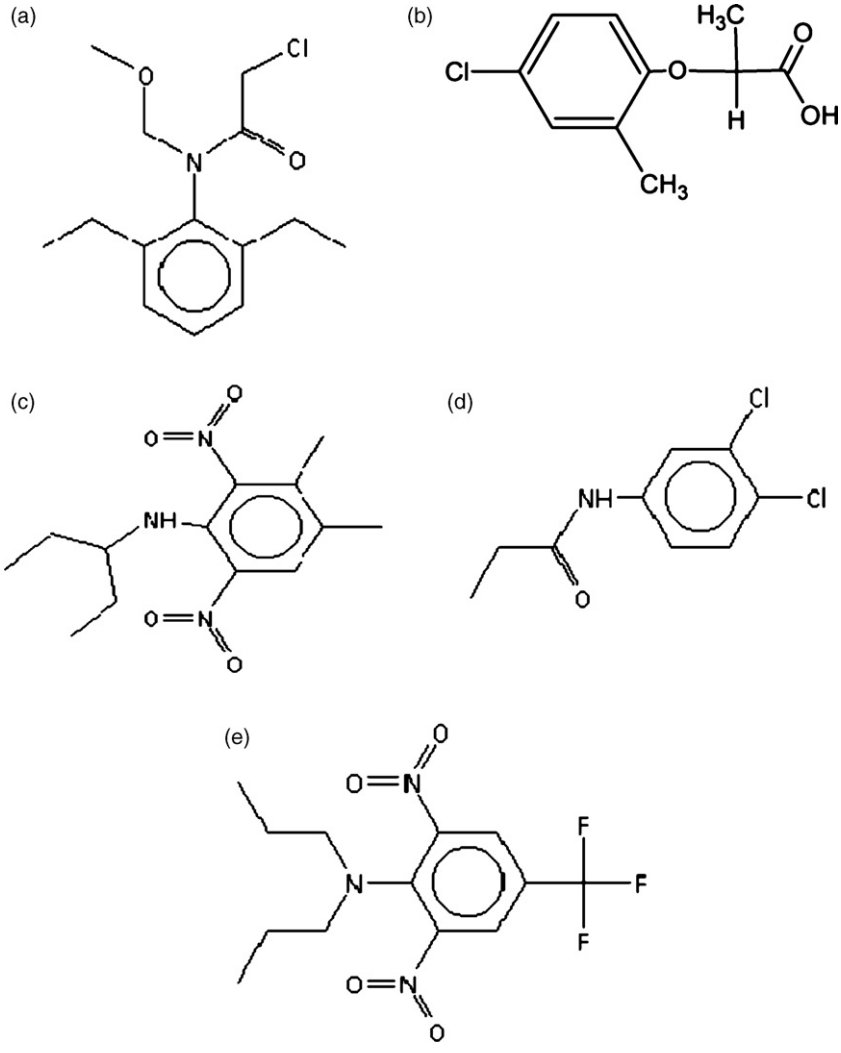

Fig. 1. Chemical formula of the five pesticides: (a) alachlor, (b) mecoprop-p, (c) pendimethanlin, (d) propanil and (e) trifluralin.

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