

Usefulness of micellar media for the quantitative analysis of phenylurea herbicides in water by photochemically-induced fluorescence

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Abstract. UV irradiation of four non-fluorescent phenylurea herbicides including linuron, diuron, isoproturon and neburon is shown to yield fluorescent photoproducts. The photochemically-induced fluorescence (PIF) properties of these herbicides in several media (water, 2-propanol and their mixtures) and aqueous micellar solutions of sodium dodecyl sulfate (SDS), and cetyltrimethylammonium chloride (CTAC) are reported. The use of micellar media enhances significantly the PIF signal relative to an aqueous solution. A PIF method is developed for the determination of the four herbicides under study, with linear dynamic ranges over about one order of magnitude, and limits of detection (LOD) between 410 and 640 ng mL⁻¹, according to the compound. Applications to the analysis of tap water and river water samples yield satisfactory recoveries (86-115 %).

Keywords. Phenylurea herbicides – micellar media – photochemically-induced fluorescence – water analysis.

Introduction

Phenylurea herbicides are widely used for the control on non-crop areas as well as for selective pre- and post-emergence weed control on crops. As a consequence, they constitute important environmental pollutants. Therefore, the development of very sensitive methods for the residue analysis of these compounds is needed.

A number of pesticides can be directly analysed by gas chromatography (GC) with various detectors. However, the urea derivatives undergo generally thermal decomposition during the analysis [1-4]. As a consequence, the direct application of GC to phenylurea herbicides is not possible because these compounds are thermally unstable, and derivatization prior to detection is requested. For this reason, high performance liquid chromatography (HPLC) with UV absorption or fluorescence detection [5-8] is preferred to GC. The proposed HPLC methods, however, suffer from a lack of specificity [9,10]. In other GC studies, the urea derivatives were hydrolysed into the corresponding anilines and then derivatized for sensitive electron capture detection [11-13].

Recently, we have applied photochemically-induced fluorescence (PIF) spectrometry to the determination of some aromatic insecticides and resolution of their binary mixtures [14,15]. In the analysis of a variety of pesticides, including neburon, HPLC postcolumn photolysis and fluorogenic labelling with OPA/2-ME, was also utilized [16]. PIF detec-

tion coupled with FIA has been proposed for the determination of a phenylurea derivative (diflubenzuron) and other aromatic pesticides [15-17]. Therefore, the combination of the PIF technique with dynamic systems such as HPLC and FIA is making progress and a great development is expected in the future.

No systematic identification of the exact nature of photoproducts formed during the pesticide photolysis reactions has been reported. However, some authors have found that, in the photodegradation pathways of phenylurea herbicides, one of the photoproducts formed is methylamine or dimethylamine [18,19]. In this respect, it was also reported that aniline and substituted anilines present fluorescence spectra similar to those of the phenylurea photodegradation products, suggesting that similar structures may be responsible for the fluorescence response observed [16].

In spite of their great analytical interest, micellar media have been seldom applied to the fluorescence or PIF analysis of pesticides [20-22]. Recently, we have proposed the use of aqueous micellar solutions to enhance the PIF signal and improve the detection of fenvalerate and deltamethrin [21] and some sulfonylurea herbicides [22].

In this paper, as a continuation of our preliminary PIF study of phenylurea herbicides in various solvents [23], we examine the usefulness of aqueous micellar media for PIF analysis of these compounds and the possible advantages of these media with respect to plain aqueous solution. We describe here a PIF method for the determination of four

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phenylurea herbicides including linuron, diuron, isoproturon and neburon (Fig. 1), based on their photolysis reaction in anionic and cationic micellar media. The method is applied to the quantitative analysis of these herbicides in natural water samples.

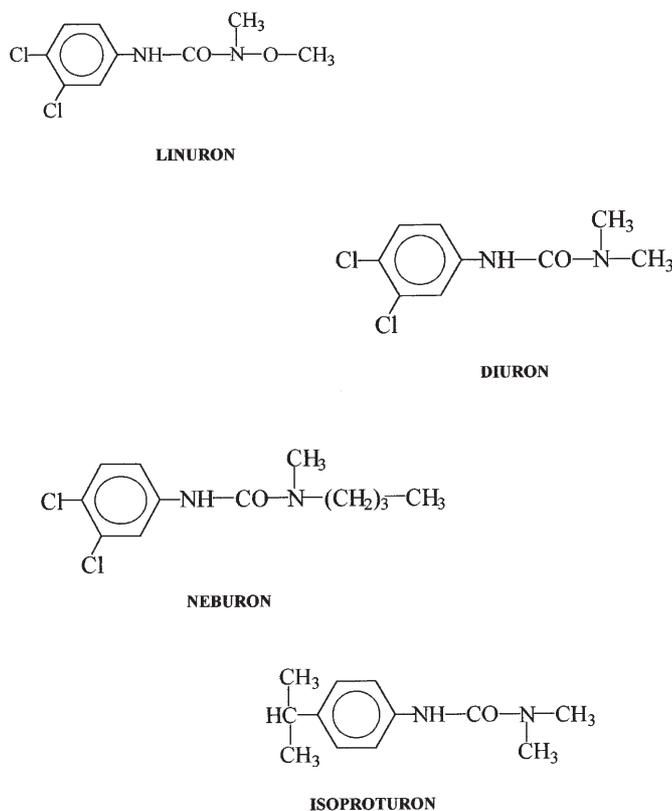


Fig. 1. Structure of the phenylurea herbicides under study.

Experimental

Reagents

Linuron (99 %, m/m), diuron (98 %, m/m), isoproturon (99 %, m/m) and neburon (99 %, m/m) were purchased from Riedel-de-Haën (Hanovre, Germany) and used as received. Cetyl trimethylammonium chloride (CTAC) 25% wt. solution in water (Aldrich), sodium dodecyl sulfate (SDS, 99 % m/m) analytical-reagent grade (Acros Organics, Geel, Belgium), spectroscopic grade 2-propanol (Merck) and 20 % v/v buffer solutions of pH 2, 5, 7 and 9 (Acros Organics, Fluka and Merck) were utilized. Distilled water was used for preparing micellar solutions.

Apparatus

All spectrofluorimetric measurements were performed on a Perkin-Elmer LS-5 luminescence spectrometer interfaced with a Geocom microcomputer, using a laboratory-made

software. An unfiltered Osram 200 W HBO high-pressure mercury lamp with an Oriel Model 8500 power supply was utilized for photolysis reactions. The photochemical set-up included a light-box consisting of a fan, the mercury lamp and a quartz lens. A standard Hellma (Mullheim, Germany) 1-cm pathlength quartz fluorescence cuvette was placed on an optical bench at 30 cm from the mercury lamp. The solutions were magnetically stirred during the UV irradiation. All spectrofluorimetric measurements were carried out at $20 \pm 1^\circ\text{C}$, using the thermostated cell holder and a Landa Model K4R thermostatic bath.

Procedure

Solution preparation

Stock solutions of the phenylurea herbicides (5×10^{-3} M) were prepared by dissolving the compound in 2-propanol. Working solutions were obtained by appropriate dilutions with distilled water. All solutions were protected against light with aluminium foil. Stock solutions of CTAC (0.01M) and SDS (0.1M) were prepared with distilled water. Working solutions were obtained by serial dilutions. Micellar solutions of the herbicides were prepared by transferring 25 or 50 μL of 2-propanolic working standard solution into a 5 mL flask, and adjusting to the marker with micellar solution, 1 mL of the optimal pH buffer solution (in some experiments) and distilled water. All working micellar aqueous solutions contained less than 1 % (v:v) of 2-propanol.

Analytical measurements and photolysis reaction

The herbicides under study did not exhibit any native fluorescence, but when herbicide micellar or aqueous solutions were irradiated with UV light, a fluorescent emission was obtained.

For the PIF analytical method, an aliquot of the micellar solution was placed in a quartz cuvette and irradiated at room temperature with UV light for a fixed time. Curves of fluorescence intensity versus UV irradiation time were constructed, at the analytical excitation (λ_{ex}) and emission (λ_{em}) wavelengths of the herbicide photoproduct, using different time periods, according to the herbicide. Linear calibration curves were obtained at these λ_{ex} and λ_{em} values, by measuring the PIF signal corresponding to the optimum irradiation time ($t_{\text{PIF}}^{\text{opt}}$), defined as the irradiation time corresponding to the maximum PIF intensity. In each case, all PIF intensity measurements were corrected for the background signal using the appropriate blanks. To optimize the analytical results, PIF measurements were carried out in triplicate and expressed as mean values.

Water sample analysis

Three aliquots (0.4, 0.6 and 0.8 mL) of stock standard solutions of tap or river water samples spiked with one of the herbicides were introduced in 5-mL volumetric flasks, in which the appropriate volume of micelle solution, 1 mL of

the pH 7 buffer solution and the required amount of distilled water were added, before irradiation and PIF measurements. No residue of the four herbicides was found in the river water samples. However, we detected in the river water samples the presence of a fluorescent species with excitation and emission maximum wavelength value ($\lambda_{\text{ex}} = 332$ nm, $\lambda_{\text{em}} = 422$ nm) relatively close to the herbicide excitation and emission maxima. The standard addition procedure was used for the recovery experiments. In order to minimize the influence of the fluorescent matter or any other dissolved substance in the water sample, a maximum percentage of 16 % (v/v) of the sample was allowed in the final volume (5 mL) of the solution to be analyzed.

Results and discussion

PIF properties

As already mentioned, we investigated previously the PIF behaviour of the four phenylurea herbicides under study, in different media, including acetonitrile, ethanol, methanol, 2-propanol, water and alcohol-water mixtures [23]. Although the UV irradiation times were found to be generally longer in 2-propanol than in an aqueous medium for all herbicides except isoproturon, we observed also that the PIF signals, measured at the $t_{\text{irr}}^{\text{opt}}$ value, were higher in the alcohols than in water [23]. However, for water analysis of herbicide residues, the use of an aqueous medium is recommended. Significant PIF enhancements in SDS and/or CTAC aqueous micellar media were reported for pyrethroid insecticides [21] and sulfonylurea herbicides [22]. Taking into account these considerations, we chose to study the effect of the above-mentioned micellar media on the PIF properties of the selected phenylurea herbicides.

The PIF excitation and emission wavelengths, $t_{\text{irr}}^{\text{opt}}$ values (corresponding to the photoproduct maximum fluorescence intensity) and relative PIF intensities (I_{F}) of the four herbicides in various micellar and non-micellar media are presented in table I. As can be seen, all compounds exhibit a marked red-shift (58-84 nm) of their PIF emission maximum in SDS and CTAC micellar solution relative to pure water, which indicates significant interactions between the phenylurea photoproduct and micelles. Except for linuron, only one fluorescent photoproduct is formed upon UV irradiation. In SDS and CTAC media, linuron photodecomposes into two different fluorescent photoproducts, emitting respectively at 314 nm ($\lambda_{\text{ex}} = 282$ nm) and 418 nm ($\lambda_{\text{ex}} = 324$ nm); the 418 nm band is used for analytical purposes, since it produces the largest PIF signal. In most cases, micellar media provide significant increases of the phenylurea herbicide PIF intensity relative to water (Tab. I). Micellar enhancement factors (MEF) defined as the ratio of the PIF relative intensity in the micellar medium and water, range between 0.8 and 16.9, according to the compound, the nature of the surfactant and pH. CTAC provided larger signal enhancements than SDS for all herbicides. The largest MEF values were found for isoproturon in CTAC, pH 7 and

Table I. PIF properties for phenylurea herbicides in several media.

Compound	Medium ^a	$\lambda_{\text{exc}}/\lambda_{\text{em}}$ ^b (nm)	$t_{\text{irr}}^{\text{opt}}$ ^c (min)	I_{F} ^d	MEF ^e
<i>Linuron</i> (5×10^{-6} M)	2-propanol	324 / 406	4	8.5	–
	H ₂ O	324 / 360	3	1.0	–
	SDS	324 / 418	10	6.1	6.1
	SDS (pH = 5)	324 / 418	10	2.9	2.9
	SDS (pH = 7)	320 / 414	8	5.0	5.0
	CTAC	324 / 418	10	6.3	6.3
	CTAC (pH = 5)	324 / 418	4	1.8	1.8
	CTAC (pH = 7)	324 / 418	8	4.1	4.1
<i>Diuron</i> (5×10^{-5} M)	2-propanol	312 / 424	8	4.0	–
	H ₂ O	312 / 350	3	1.1	–
	SDS	318 / 430	25	1.1	1.0
	SDS (pH = 5)	318 / 430	20	1.0	0.9
	SDS (pH = 7)	318 / 430	22	1.3	1.2
	CTAC	314 / 434	18	1.3	1.2
	CTAC (pH = 5)	318 / 430	12	1.1	1.0
	CTAC (pH = 7)	324 / 430	16	1.2	1.1
<i>Isoproturon</i> (5×10^{-5} M)	2-propanol	321 / 436	6	42.0	–
	H ₂ O	330 / 370	8	1.0	–
	SDS	300 / 436	24	8.3	8.3
	SDS (pH = 5)	300 / 436	30	7.6	7.6
	SDS (pH = 7)	300 / 436	25	9.3	9.3
	CTAC	306 / 436	25	14.6	14.6
	CTAC (pH = 5)	306 / 436	30	11.9	11.9
	CTAC (pH = 7)	306 / 436	25	16.9	16.9
<i>Neburon</i> (5×10^{-5} M)	2-propanol	312 / 422	12	1.7	–
	H ₂ O	306 / 350	4	1.2	–
	SDS	308 / 432	20	1.0	0.8
	SDS (pH = 5)	308 / 432	20	1.1	0.9
	SDS (pH = 7)	308 / 432	20	1.4	1.1
	CTAC	308 / 432	20	1.5	1.2
	CTAC (pH = 5)	308 / 434	20	1.2	1.0
	CTAC (pH = 7)	308 / 434	20	1.7	1.4

^a [CTAC] = 8×10^{-3} M; [SDS] = 8×10^{-2} M.

^b λ_{ex} and λ_{em} = analytical PIF excitation and emission wavelength.

^c $t_{\text{irr}}^{\text{opt}}$ = optimum irradiation time, corresponding to the maximum PIF intensity (I_{F}).

^d I_{F} = relative maximum PIF intensity, corrected for the solvent (blank) signal and normalized to the lowest PIF signal for each compound.

^e MEF = micellar enhancement factor, corresponding to the ratio of the PIF relative intensity in the micellar medium and water.

linuron in CTAC, whereas diuron and neburon yielded MEF values only slightly larger than unity in CTAC and close to one in SDS.

Photolysis kinetic study

To evaluate the kinetics of the fluorophore formation, the evolution of PIF intensity with UV irradiation time was investigated in micellar media. Phenylurea herbicides are naturally non-fluorescent whereas a fluorescent band appears upon UV irradiation, indicating the formation of fluorescent photoproducts. The effect of UV irradiation on the

fluorescence intensity depends on the type of derivative, pH and micellar medium used. In most cases, the fluorescence signal increased initially with time, reaching a maximum value (plateau) and decreasing afterwards. Examples of this kinetic behaviour in various micellar media and pH are given for diuron (CTAC medium, pH 5), linuron (SDS medium, pH 7) and isoproturon (CTAC medium, pH 7) in figure 2a (curve A), 2b and 2c, respectively. However, in a few cases, such as the photolysis of neburon in SDS medium, the kinetic is characterised by a continuous increase of the PIF signal with time and no well-defined maximum value (Fig. 2a, curve B). These two types of kinetic curves can be explained by the existence of two distinct mechanisms of photolysis. The first type corresponds to a two-step mechanism, including the formation of fluorescent photoproduct(s) and subsequent photodegradation of the photoproduct(s) into non-fluorescent products. The second type of curve indicates that fluorescent photoproduct(s) are progressively formed. These kinetics are similar to those previously obtained for the photolysis of several aromatic insecticides [14] and sulfonylurea herbicides [22]. Also, it must be pointed out that the optimum irradiation time values are significantly longer in aqueous micellar media than in water (Tab. I).

pH effects

Phenylurea herbicides are known to be hydrolyzed in acid and basic media. With a view on possible applications to real environmental samples for which the pH value must be fixed, we investigated the pH effect on the PIF signal. Two buffer solutions of pH 5 and 7 were tested because these pH values are close to those measured for the unbuffered aqueous solutions of the herbicides under study. Linuron PIF intensity decreased in both SDS and CTAC buffer solution relative to the corresponding unbuffered micellar solutions, whereas in the case of isoproturon and neburon the strongest PIF signals were obtained in the pH 7 buffer for both media. The pH behaviour of diuron depended on the type of micelle: in SDS, the highest PIF signal was measured at pH 7, while in CTAC the PIF intensity was slightly higher in the unbuffered solution. Since the strongest PIF signals were recorded for most herbicides in a pH 7 buffer micellar solution, this medium was selected as a compromise for further analytical studies. The change of PIF signal with the pH of the micellar solution can be attributed to the photolysis of the phenylurea herbicide under study into ionizable, fluorescent photoproducts. Indeed, assuming that one of the photoproduct prototropic species is more strongly fluorescent than the other, the PIF signal intensity would be expected to depend on the percentage of this species in the micellar medium at the given pH, in relation with the photoproduct pKa.

SDS and CTAC concentration effect

As previously noted for other pesticides [21], the addition of increasing surfactant concentrations to the phenylurea herbicide solution produced an enhancement of the PIF

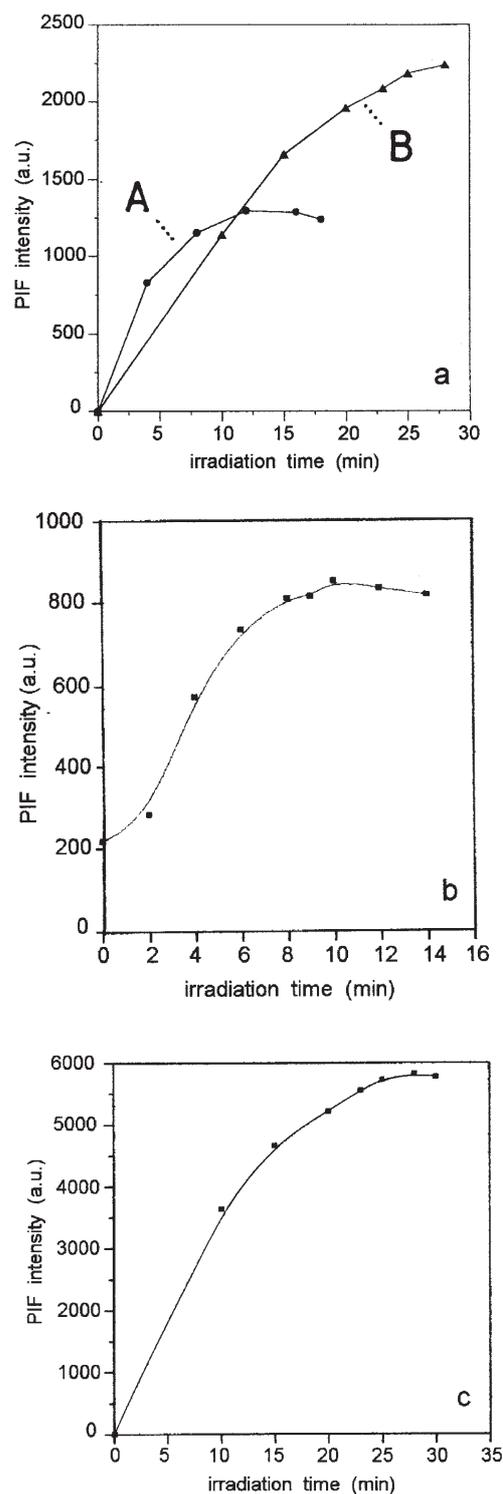


Fig. 2. a. Effect of the UV irradiation time on the PIF intensity of (A) diuron (5×10^{-5} M) in a 5×10^{-3} M CTAC aqueous solution (pH 5) and (B) neburon (5×10^{-5} M) in a 5×10^{-2} M SDS aqueous solution (pH 7). b. Effect of the UV irradiation time on the PIF intensity of linuron (5×10^{-6} M) in a 5×10^{-2} M SDS aqueous solution (pH 7). c. Effect of the UV irradiation time on the PIF intensity of isoproturon (5×10^{-5} M) in a 5×10^{-3} M CTAC aqueous solution (pH 7).

signal relative to water. This increase of the PIF intensity occurs at surfactant concentrations close to the critical micellar concentration (CMC) value. It may be attributed to the decrease of the vibrational motions and increase of the rigidity of photoproduct molecules when they become included in the micelle core. Fig. 3 shows the plots of linuron PIF intensity *versus* the SDS and CTAC concentrations; similar curves are obtained for diuron, isoproturon and neburon. These results suggest that the highest possible surfactant concentration should be used to provide the strongest fluorescence emission. For the herbicides under study, SDS and CTAC concentrations of respectively 8×10^{-2} M and 8×10^{-3} M corresponding to about 9.3 times and 6.1 times the respective CMC values were chosen.

Stability of the photoproducts

The influence of the time course on the PIF signal was studied after optimization of the experimental variables. We found that, for all herbicides, the photoproducts remain stable during at least 30 hours after irradiation, when micellar solutions are kept in the dark.

Analytical figures of merit

In order to evaluate the analytical usefulness of our approach, the analytical figures of merit were determined in the optimal conditions and micellar media listed in table II. Linear calibration plots were established for all phenylurea herbicides over about one order of magnitude with a satisfactory linearity, as shown by the determination coefficients (r^2) larger than 0.99 (Tab. III). The reproducibility of the measurements was satisfactory, as shown by the Relative Standard Deviation (RSD) ranging from 3.9 to 6.1 %. Limits of detection (LOD), defined according to the criterium of Clayton [24] range from 410 to 640 ng/mL, according to the compound (Tab. III). Although these LOD values are higher than those obtained previously by the PIF method in 2-propanol: water mixtures [23b], the use of aqueous micellar media appears to be more convenient for the analysis of phenylurea herbicides in real water samples. Indeed, the cost

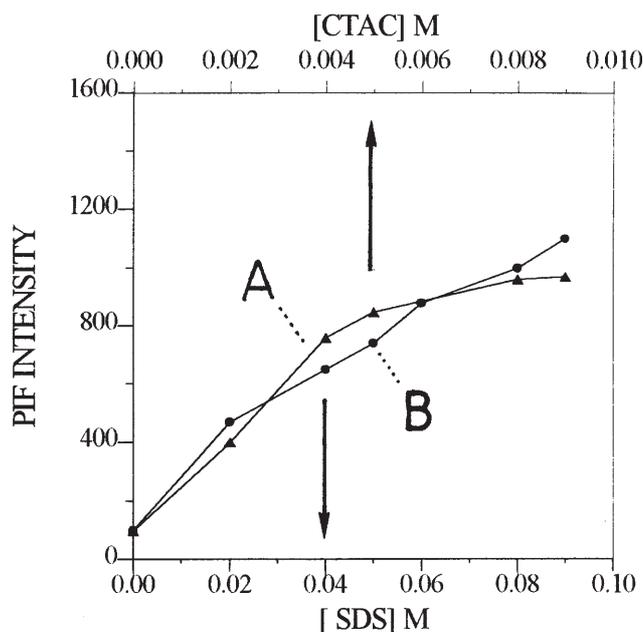


Fig. 3. Influence of CTAC (A) and SDS (B) concentrations on the PIF intensity of 5×10^{-6} M linuron ($t_{ir} = 8$ min).

Table II. PIF optimal analytical conditions.

Compound	Medium	pH	$\lambda_{exc}/\lambda_{em}$ (nm)	t_{ir}^{opt} (min)
Linuron	SDS	7	320/414	8
Diuron	SDS	7	318/430	22
Isoproturon	CTAC	7	306/436	25
Neburon	CTAC	7	308/434	20

of the PIF method is lower when using surfactants instead of 2-propanol and the pretreatment procedure for water sample analysis is more simple in the presence of surfactants.

Table III. Analytical figures of merit for the determination of phenylurea herbicides.

Compound	Concentration range ($\mu\text{g.mL}^{-1}$)	Slope	r^2 ^a	LOD ^b (ng.mL^{-1})	Analytical sensitivity ^c (ng.mL^{-1})	RSD (%)
Linuron	0.87 - 6.23	423.2	0.995	410	170	4.0 ^d
Diuron	0.70 - 6.99	145.2	0.990	640	270	6.1 ^e
Isoproturon	0.52 - 6.19	721.2	0.994	420	180	4.7 ^f
Neburon	0.69 - 5.5	240.4	0.992	440	190	3.9 ^g

^a r^2 = determination coefficient.

^b Limit of detection according to the criterium of Clayton [24].

^c Analytical sensitivity defined according to [25].

^d Calculated for a concentration of $2.49 \mu\text{g mL}^{-1}$.

^e Calculated for a concentration of $2.33 \mu\text{g mL}^{-1}$.

^f Calculated for a concentration of $2.06 \mu\text{g mL}^{-1}$.

^g Calculated for a concentration of $2.75 \mu\text{g mL}^{-1}$.

Analytical applications

To show the analytical applicability of the proposed method to authentic samples, recovery experiments of the phenylurea herbicides under study were performed on spiked tap water and Seine River water samples. Tap water samples were free of any fluorescent dissolved species and a pH of 7.95 was found for the samples. Seine River samples were filtered with a Whatman N°1 filter paper in order to eliminate the suspended organic matter. A pH value of 8.18 was found for these samples. Tap water and river water samples were spiked with 19.93, 34.96, 20.63 and 13.76 $\mu\text{g}\cdot\text{ml}^{-1}$ of linuron, diuron, isoproturon and neburon, respectively. The spiked solutions were then ultrasonically stirred for 5 min before being kept in the dark, and used as stock standard solutions of natural water. Three aliquots (0.4, 0.6 and 0.8 ml) of these stock standard solutions of water samples were introduced in 5-mL volumetric flasks as described in the experimental section. Table IV summarizes the results of three replicate analyses. The average recovery values, ranging from 86 % to 115 % (river water) and 91.2 % to 112.8 % (tap water), can be considered as satisfactory. Application of the student t-test to these recovery data indicates that t values are comprised between 0.13 and 3.86 for most results. These values are less than the theoretical value of 4.303 (2 degrees of freedom and confidence level of 95 %), which confirms the validation of the proposed method for the determination of the selected herbicides in water samples.

Conclusion

We have shown in this work that UV irradiation of the phenylurea herbicides in micellar media yields strongly fluorescent photoproducts. The use of micellar media leads to significant enhancements of the photochemically induced fluorescence (PIF) signals of the herbicides and to increases of the optimum irradiation times, relative to plain water. Using this photochemical approach, we have established a simple and reproducible PIF method, suitable for residue analysis of these phenylurea herbicides in spiked tap water and river water samples. Low cost equipment is needed; no complicated pretreatment and no isolation of the photoproducts are requested for analytical applications. Presently, in our laboratories, we consider the possibility of combining PIF detection in micellar media with flow injection analysis (FIA) and on-line photoreaction, in order to improve the speed and convenience of our approach for quantitation of phenylurea herbicides in natural waters and in commercial formulations. Also, we will try to apply derivative PIF spectrometric methods and/or partial least squares (PLS) multivariate calibration techniques to the resolution of mixtures of these herbicides.

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Table IV. Determination of phenylurea herbicides in tap water and river water samples.

Compound	Concentration ($\mu\text{g}\cdot\text{mL}^{-1}$)		Recovery %
	Added	Found ($E \pm s$) ^a	
River water			
<u>Linuron</u>	1.59	1.52 \pm 0.02	95.6
	2.39	2.18 \pm 0.05	91.2
	3.19	2.72 \pm 0.04	86.0
<u>Diuron</u>	2.80	2.81 \pm 0.15	100.4
	4.20	4.13 \pm 0.04	98.3
	5.59	5.29 \pm 0.09	94.6
<u>Isoproturon</u>	1.65	1.56 \pm 0.01	94.5
	2.48	2.30 \pm 0.01	92.7
	3.30	3.03 \pm 0.03	91.8
<u>Neburon</u>	1.10	1.27 \pm 0.02	115.4
	1.65	1.75 \pm 0.04	106.0
	2.20	2.12 \pm 0.06	96.4
Tap water analysis			
<u>Linuron</u>	1.59	1.45 \pm 0.02	91.2
	2.39	2.18 \pm 0.02	91.2
	3.19	2.98 \pm 0.20	93.4
<u>Diuron</u>	2.80	2.84 \pm 0.04	101.4
	4.20	4.21 \pm 0.09	100.2
	5.59	5.56 \pm 0.03	99.5
<u>Isoproturon</u>	1.65	1.75 \pm 0.07	106.1
	2.48	2.53 \pm 0.06	102.0
	3.30	3.26 \pm 0.10	98.8
<u>Neburon</u>	1.10	1.24 \pm 0.02	112.7
	1.65	1.60 \pm 0.01	97.0
	2.20	2.09 \pm 0.05	95.0

^a E = mean concentration (average of three replicates); s = standard deviation.

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