

# Photochemically-Induced Fluorescence Properties of Two Benzoyl- and Phenylurea Pesticides and Determination in Natural Waters

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**Abstract** A photo-induced fluorescence (PIF) method was developed for the determination of two benzoyl- and phenylurea pesticides, namely diflubenzuron (DFB) and fenuron (FEN). The photoconversion under UV irradiation of both pesticides into strongly fluorescent photoproducts was performed in several media (methanol, ethanol, acetonitrile, pH4 aqueous solution and pH4 water–methanol (30:70, v/v) mixture). PIF parameters were optimized. Analytical figures of merit for the PIF determination of DFB and FEN were satisfactory, with rather wide linear dynamic range (LDR) values of one to two orders of magnitude, relatively low limit of detection (LOD) values of, respectively, 9–24 ng/mL for DFB and 1–28 ng/mL for FEN, and limit of quantification (LOQ) values of, respectively, 30–80 ng/mL for DFB and 4–95 ng/mL for FEN, according to the medium. Relative standard deviation (RSD) values were in the range 1.7–5.6 %. PIF was validated by comparing its analytical performances to those of a standard UV absorption spectrophotometric method. The optimized PIF method was applied to the quantitative analysis of both pesticides in various spiked natural water samples collected in a Senegal agricultural area by the standard addition procedure prior to extraction steps in dichloromethane, with satisfactory mean recovery percentage values (97.0–105.3 for DFB and 98.3–102.8 % for FEN). An interference study of foreign species, including pesticides and

inorganic ions, likely to be present in natural waters, was also carried out.

**Keywords** Diflubenzuron · Fenuron · Pesticides · Photo-induced fluorescence · Water analysis · Interference studies

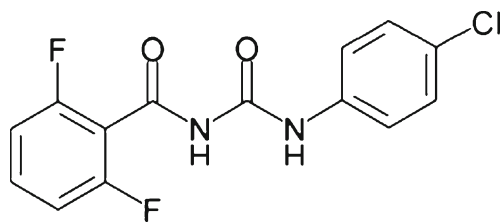
## Introduction

Diflubenzuron (DFB) and fenuron (FEN) belong, respectively, to the benzoylurea and the phenylurea families, which constitute an important group of pesticides that are widely used in agriculture. DFB is a non systemic insect growth regulator which acts by inhibiting the formation of chitin cuticles, either blocking the insect moulting process or acting at hatching of eggs [1]. The inherent low toxicity of DFB for mammalians, birds and fish and its clear selectivity with respect to many non-target insects has encouraged its commercial development [1, 2]. FEN is a non-selective, systemic pre- and post-emergence herbicide used for the control of deep-rooted weeds and annual grasses in crops [1, 3]. However, FEN is rapidly degraded in the environment by hydrolysis and/or photolysis into many metabolites of which some are classified as mutagens by the National Cancer Institute and the Cancer Assessment Group of the US Environmental Protection Agency [4–7]. Because of their intensive application in agriculture, both pesticides constitute important pollutants and can be found at trace levels in different environmental matrices. We were especially concerned by the development of rapid, selective and sensitive methods for the determination of DFB and FEN (Fig. 1) residues in Senegalese natural waters, due to their extensive use in the rice crops of the Senegal River valley.

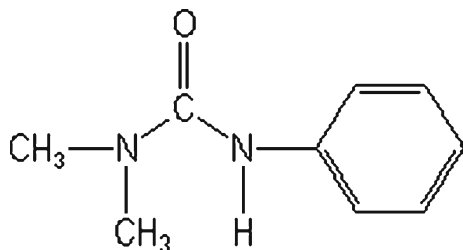
Several authors have already used different analytical approaches in order to determine DFB, FEN and other phenyl-

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Diflubenzuron (DFB)



Fenuron (FEN)

**Fig. 1** Molecular structures of diflubenzuron (DFB) and fenuron (FEN)

or benzoylurea pesticides in soil, water, fruit and vegetables [8–18]. Both gas chromatography (GC) and high pressure liquid chromatography (HPLC) have been applied. For DFB, direct GC determination was not feasible because of its thermal decomposition into metabolites, such as 2,6-difluorobenzamide, 4-chloroaniline and 4-chlorophenyl isocyanate [8], whereas indirect GC required derivatization processes with subsequent electron-capture (EC) and MS detection [9–13]. Therefore, HPLC remained the major analytical technique developed for DFB and FEN. For instance, Carabias-Martinez et al. [3] simultaneously determined ten phenyl- and sulphonylurea herbicides, including FEN, by liquid chromatography (LC) with UV diode array detection (DAD) or mass spectrometric (MS) detection, and verified their applicability in natural water samples after applying a pre-concentration step based on solid-phase extraction (SPE). These authors concluded that both methods were suitable, with measurable herbicide concentrations below  $0.1 \mu\text{g L}^{-1}$ .

HPLC have been also used for the quantification of DFB in water, fruits and food with different detection systems such as UV DAD, electrochemistry, MS, fluorescence and chemiluminescence [2, 14–16, 18]. Rodriguez et al. [2] applied LC with on-line UV DAD and electrochemical detection (ED) to improve the sensitivity in the determination of DFB and its main metabolites in forestry matrices (pine needles). Low limit of detection (LOD) values of  $2.0\text{--}25.2 \mu\text{g L}^{-1}$  for DAD and  $0.07\text{--}1.8 \mu\text{g L}^{-1}$  for ED were obtained with recovery percentages higher than 90 % in most cases. The combination of DAD and ED permitted to improve the advantages of both detection systems.

It is worthwhile to note that Martinez Galera et al. [14] recently reported the first analytical application of the luminol

chemiluminescence reaction for the sensitive detection of two benzoylurea insecticides, including DFB and triflumuron. They determined both pesticides in tomato samples by coupling LC with post-column photoderivatization and detection based on this chemiluminescence reaction. The optimised and validated method led to a LOD value of  $0.025 \mu\text{g mL}^{-1}$ , and a limit of quantification (LOQ) of  $0.05 \mu\text{g mL}^{-1}$ , lower than the maximum residue levels established by the European Union (EU) for drinking water ( $0.1 \mu\text{g mL}^{-1}$ ). Also, Gil Garcia et al. [15] developed an on-line pre-concentration and LC-fluorescence detection technique after photo-induced fluorescence post-column derivatization, allowing them to estimate trace levels lower than  $0.1 \mu\text{g L}^{-1}$  of five benzoylureas, including DFB, in ground water samples and to avoid interferences caused by co-extracted compounds. Another approach was based on the application of multi-residue methods for the analysis of large numbers of pesticides. For example, Ferrer and Thurman [16] reported the use of LC-time-of-flight (TOF) – MS for the identification and determination of 101 pesticides, including phenylureas, in food and water samples, whereas Bedendo et al. [18] evaluated the potential of a procedure involving hollow fibre microporous membrane liquid-liquid extraction and detection by LC with electrospray-tandem-MS detection for the quantitative analysis of 18 pesticides belonging to different classes, including DFB, in industrial and fresh orange juices. The obtained limits of detection were in compliance with the regulations on food established by the EU directive. A selective and rapid, but poorly sensitive,  $^{19}\text{F}$  nuclear magnetic resonance (NMR) spectroscopic analytical procedure was also developed by Talebpour et al. to quantify residues of DFB in fruit juices, with a rather high LOD of  $6.0 \mu\text{g mL}^{-1}$  and recovery values of 92–96 % [19].

In spite of the analytical interest of the above-mentioned methods from the standpoint of selectivity and/or sensitivity, most of them involve relatively sophisticated and time-consuming procedures. Therefore, more simple, rapid and cheaper analytical approaches are needed for determining particular pesticides in the environment. Among these approaches, fluorescence analysis of pesticides is rather limited by the fact that most pesticides are not naturally fluorescent and have to be first converted into fluorescent species by various, often long and/or complex processes. However, a number of authors have investigated the photodegradation of pesticides, and have shown that, upon UV irradiation, pesticides are more or less rapidly photodecomposed into a variety of photoproducts [20–24]. Therefore, taking advantage of this photoreactivity of pesticides, an alternative method, so-called photo-induced fluorescence (PIF), which is based on the photochemical transformation of a non- or weakly-fluorescent analyte into strongly-fluorescent photoproduct(s), has been developed as a simple, rapid, sensitive and cheap tool for the determination of non- or weakly fluorescent pesticides [15,

24–35]. As pointed out in several reviews on this topic [24, 32, 35], the PIF detection system can be used either in stationary solution, or in the dynamic mode, combined with HPLC or flow injection analysis (FIA).

In this paper, we developed a simple PIF method in stationary liquid solution for the determination of DFB and FEN. We evaluated the effect of various media in order to enhance the PIF response, and we optimized several parameters such as the solvent, pH and irradiation time. We examined the analytical figures of merit of PIF in various media, and we applied the proposed PIF method to the quantitative analysis of both pesticides in spiked tap water and natural water samples collected in a Senegal agricultural area. In order to validate the PIF method, we compared the analytical performances as well as the recovery values with those obtained by UV absorption spectrophotometry, used as a standard method. An interference study of foreign species, including pesticides and inorganic ions, likely to be present in Senegal natural waters, was also carried out by means of PIF.

## Experimental

### Reagents

Technical-grade diflubenzuron (DFB - purity=99 %) and fenuron (FEN—purity=99.6 %) were, respectively, obtained from Dr Ehrenstorfer GmbH (Augsburg, Germany) and from Sigma-Aldrich, and used as received. Spectroscopic grade solvents including ethanol, methanol, acetonitrile and dichloromethane were purchased from Prolabo (France). De-ionized water was used for preparing the binary mixtures.

### Apparatus

All fluorescence measurements were performed at room temperature on a Kontron SFM-25 spectrofluorimeter, interfaced with a microcomputer. An Osram 200-W high-pressure mercury lamp with an Oriel 8000 power supply was used for the 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 path-length quartz fluorescence cell was placed on an optical bench at 30 cm from the mercury lamp. Ultraviolet–visible (UV–VIS) absorption spectral measurements were realized at room temperature with a UV–VIS absorption spectrophotometer Lambda 10 model, utilizing a software Winlab.

### Procedure

#### *Stock Solutions Preparation*

Stock standard solutions of DFB or FEN ( $10^{-3}$  M) were freshly prepared by exactly weighting and dissolving the corresponding compounds in methanol. The working standard solutions were obtained by diluting the stock standard solution in the appropriate solvent or mixture. All solutions were protected against light with aluminium foil to avoid any decomposition and stored in a refrigerator.

#### *PIF and UV–VIS Absorption Analytical Measurements and Photolysis Reactions*

An aliquot of the DFB or FEN solutions was placed in a quartz absorption or fluorescence cell. The UV–VIS absorption spectral analytical measurements were performed in the different media under study. In the case of PIF, the solutions were irradiated with UV light for different times at room temperature. The PIF intensity values were recorded at the analytical excitation and emission wavelengths of the DFB or FEN photoproduct, and curves of PIF intensity versus UV irradiation time were constructed at the optimum excitation and emission wavelengths in the various media, in order to evaluate the optimum irradiation time, corresponding to the maximum PIF signal. In all cases, the PIF intensity measurements were corrected for the background signal using the appropriate blanks. PIF signals were carried out in triplicate and expressed as mean values to optimize the analytical results.

#### *Standard Addition and Direct Spiking Procedures for the Analytical Applications*

300-mL natural water samples were collected in 0.5-L amber, glass bottles from well, river, draining and pond waters, located in an agricultural area of the Senegal River valley, during the period of August 2013. All samples were filtered through a quartz filter in order to eliminate the suspended organic matter, and stored at 4 °C. We proceeded to a liquid-liquid extraction, using dichloromethane as extracting solvent, and then, we applied either the standard addition procedure or the direct spiking procedure.

In the case of the standard addition procedure, performed with the PIF method, the filtered water samples were spiked in 10-mL flasks with standard solutions of DFB ( $150 \text{ ng mL}^{-1}$ ) or FEN ( $25 \text{ ng mL}^{-1}$ ). Then, five aliquots of 5-mL portions of these spiked water samples were introduced into five flasks, and increasing concentrations of the pesticide standard solutions, respectively from 50 to  $600 \text{ ng mL}^{-1}$  for DFB, and from 13 to  $812 \text{ ng mL}^{-1}$  for FEN, were added into four flasks, the fifth one corresponding to the blank. Flasks were adjusted to

the mark with a pH 4 30/70, *v/v* water/methanol mixture for DFB, and with ethanol for FEN.

For the direct spiking procedure applied to the PIF method, 10-mL portions of filtered water samples were spiked with three concentrations for DFB (50, 100 and 150 ng/mL), and for FEN (10, 50 and 100 ng/mL). All solutions were shaken three times with 10 mL of dichloromethane during 10 min each. The combined organic phases were dried, by passing through anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then evaporated to dryness. The residues were dissolved in 5 mL of a pH 4 30/70, *v/v* water/methanol mixture for DFB, and of ethanol for FEN.

The PIF signal was measured at the maximum emission wavelength after irradiation at the optimum time, whereas for the UV–VIS absorption method, the absorbance measurements were performed at the maximum wavelength.

## Results and Discussion

### DFB and FEN Photo-Induced Fluorescence Spectral Properties

DFB and FEN (Fig. 1) were naturally non-fluorescent in the different media under study. But, under UV irradiation, they were photolyzed into strongly fluorescent photoproduct(s), the photo-induced fluorescence intensity progressively increasing with the irradiation time. FEN and DFB were found to be soluble, respectively, in water and in methanol. In order to choose an optimized medium for the PIF determination of both pesticides, we decided to investigate the influence of water percentage on the DFB PIF signal in water–methanol binary mixtures, and also the pH effect in a purely aqueous medium for FEN and in a water/methanol mixture for DFB. Afterwards, the PIF study was performed in different organic solvents including ethanol, methanol, acetonitrile, as well as in water/methanol 30/70, *v/v*, pH 4 water/methanol 30/70, *v/v* mixtures and in pH 4 aqueous solution. The PIF spectral properties of both pesticides are reported in Table 1. As an example, the DFB PIF excitation and emission spectra were provided in Fig. 2 for four media, namely ethanol, methanol, water/methanol 30/70, *v/v* and pH 4 water/methanol 30/70, *v/v* mixtures. As can be seen, the PIF excitation and emission spectra were rather well resolved and presented only one single, wide band.

In the case of DFB, no important shift of the PIF excitation and emission maximum wavelengths occurred with the medium, but the PIF signal intensity and irradiation time significantly varied according to the medium (Fig. 2). The shape of the PIF excitation and emission spectra was similar in all media, the PIF excitation maximum wavelength being located at about 331–333 nm, whereas the emission maximum wavelength occurred, respectively, at 400 nm in methanol and

ethanol, and at 405 nm in water/methanol 30/70, *v/v* and pH 4 water/methanol 30/70, *v/v* mixtures. The DFB PIF signal was about 1.7–2.0 times higher in water/methanol 30/70, *v/v* and pH 4 water/methanol 30/70, *v/v* mixtures than in ethanol (Table 1 and Fig. 2).

In contrast, for FEN, significant red-shifts of the PIF excitation and emission maximum wavelengths were observed in methanol, ethanol and acetonitrile, relative to pH 4 aqueous solution (Table 1). Indeed, the excitation maximum wavelengths varied from 300 nm in methanol and ethanol and 320 nm in acetonitrile to only 282 nm in pH 4 aqueous solution, whereas the emission ones ranged from 415 nm in methanol and ethanol and 395 nm in acetonitrile to 343 nm in pH 4 aqueous solution. Moreover, the FEN PIF intensity value was about 2.0–7.7 times larger in ethanol than in methanol, pH 4 aqueous solution and acetonitrile.

In order to evaluate the influence of water in water–methanol binary mixtures, we investigated the effect of water percentage on the DFB PIF intensity, measured at the optimum irradiation time value ( $t_{\text{irr}}^{\text{opt}}=30$  min). PIF intensity was found to rapidly increase with the percentage of water (from 0 to 30 %), reaching a maximum value for 30 % of water (70 % of methanol), and then progressively decreased, when the percentage of water increased from 30 to 70 % (Fig. 3). An analogous behaviour, concerning the effect of water percentage on the PIF intensity in binary water–alcohol and water–dimethylsulfoxide (DMSO) mixtures and the existence of a PIF intensity maximum around 70–80 % water, has been observed by several authors in PIF studies of other benzoylurea insecticides, including flufenoxuron, lufenuron, hexaflumuron and triflumuron, in technical formulations and river water samples [31], and of photoreactive, non-steroidal anti-inflammatory drugs (NSAIDs), such as meclofenamic acid and niflumic acid, in pharmaceutical formulations and in urine [36, 37]. Therefore, our results confirmed that the variation of the polarity of water–methanol binary mixtures with water content played an important role in the increase of the PIF signal and in the optimization of PIF method.

We also studied the effect of pH on the DFB and FEN PIF signals, respectively, in water/methanol 30/70, *v/v* mixture and in aqueous solution. The DFB and FEN pH curves presented the same shape. Indeed, the curves of PIF intensity versus pH, established in the pH 1.0–12.0 region, displayed two maxima at about pH 4 and 10, and at about pH 4 and 8, for, respectively, DFB and for FEN, in accordance with the existence of two protonation sites in the pesticide molecular structures. In Fig. 4, we showed an example of a PIF intensity curve vs. pH for FEN. These curves were characterized by an initial increase of the PIF signal with increasing pH, a maximum being reached at pH 4 for both pesticides, and, afterwards, by a PIF signal decrease, before reaching a second maximum at about pH 10 and 8, respectively, for DFB and FEN.

**Table 1** PIF and UV–VIS absorption spectral properties and analytical figures of merit of DFB and FEN in organic solvents and in aqueous media

PIF										
Pesticide <sup>a</sup>	Solvent	$\lambda_{ex}/\lambda_{em}$	$t_{irr}^{opt}$ (min)	$I_f^c$	LOD <sup>d</sup> (ng/mL)	LOQ <sup>e</sup> (ng/mL)	$r^{2f}$	LDR (ng/mL)	RSD (%)	
DFB	pH 4 Water/MeOH (30/70, v/v)	331/405	30	2	9	30	0.998	75–1,500	4.5	
	Water/MeOH (30/70, v/v)	331/405	30	1.8	16	53	0.998	150–1,500	3.7	
	Methanol	331/400	30	1.7	19	62	0.995	150–1,500	1.7	
	Ethanol	333/400	20	1	24	80	0.994	150–3,000	5.6	
FEN	Methanol	300/415	10	5.2	2	7	0.999	25–1,624	2.5	
	Ethanol	300/415	10	7.7	1	4	0.999	12–812	4.2	
	Acetonitrile	320/395	20	2.1	14	47	0.999	100–3,248	2.2	
	pH 4 aqueous solution	282/343	20	1	28	95	0.999	200–6,496	5.2	
UV–VIS absorption										
Pesticide	Solvent	$\lambda_{abs}$ (nm)	$\epsilon^j$ (L.mol <sup>-1</sup> .cm <sup>-1</sup> )	LOD <sup>d</sup> (ng/ml)	LOQ <sup>e</sup> (ng/ml)	$r^{2f}$	LDR (ng/mL)	RSD (%)		
DFB	Methanol	270	16,895±680	29	96	0.999	300–15,000	4.0		
	pH 4 water/MeOH (30/70, v/v)	270	17,515±355	35	117	0.997	300–15,000	2.0		
	Ethanol	270	18,848±985	33	110	0.995	300–15,000	5.2		
	Acetonitrile	267	18,352±570	27	89	0.999	300–15,000	3.1		
FEN	Methanol	252	14,090±370	52	173	0.999	406–8,120	2.6		
	Ethanol	252	17,220±870	36	120	0.998	162–8,120	0.5		
	Aetonitrile	255	18,080±310	32	108	0.998	162–8,120	1.7		
	pH 4 aqueous solution	250	11,680±435	75	250	0.997	406–8,120	3.7		

*r* correlation coefficient

*LDR* linear dynamic range

*RSD* relative standard deviation

$\lambda_{abs}$  absorption maximum wavelength

$\epsilon$  molar absorption coefficient

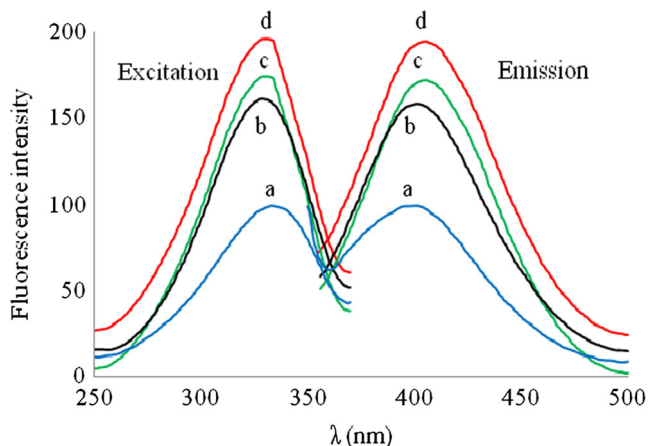
<sup>a</sup> Pesticide concentrations =  $5 \times 10^{-6}$  M

<sup>b</sup>  $t_{irr}^{opt}$  optimum irradiation time

<sup>c</sup> Relative PIF intensity, normalized relative to the PIF intensity in ethanol for DFB and in pH 4 aqueous solution for FEN

<sup>d</sup> *LOD* Limit of detection, defined as the concentration of analyte giving a signal-to-noise ratio (S/N) of 3 (IUPAC criterion)

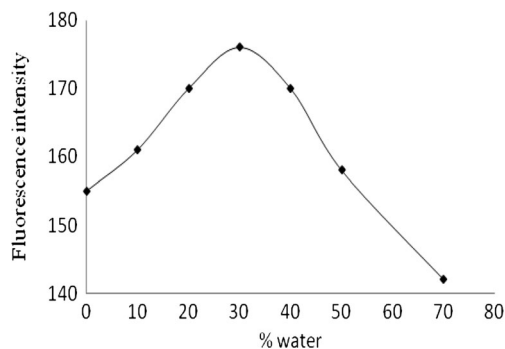
<sup>e</sup> *LOQ* Limit of quantification, defined as the concentration of analyte giving a S/N ratio of 10 (IUPAC criterion)



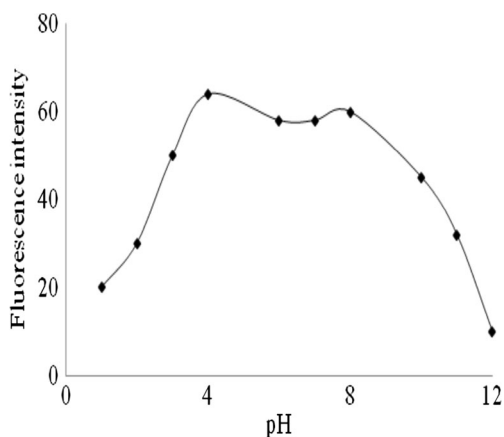
**Fig. 2** PIF excitation and emission spectra of  $5 \times 10^{-6}$  M DFB solutions, recorded at the optimum irradiation time in: **a** ethanol; **b** methanol; **c** water–methanol (30 %/70 %, v/v); **d** pH 4 water–methanol (30 %/70 %, v/v)

Photolysis Kinetic Study

We monitored the photodegradation reactions of DFB and FEN by following the change of PIF signal, recorded at the pesticide excitation and emission maximum wavelengths, as a

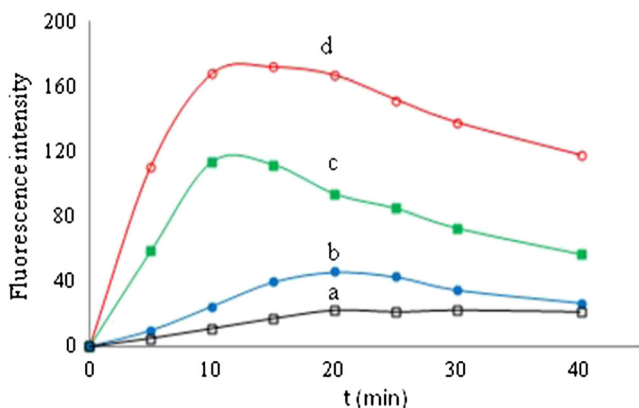


**Fig. 3** Effect of the variation of water percentage on the PIF signal of DFB ( $5 \times 10^{-6}$  M) water–methanol mixtures at optimum irradiation time ( $t_{irr}^{opt} = 30$  min)



**Fig. 4** pH effect on the PIF intensity of FEN ( $2 \times 10^{-5}$  M) aqueous solutions

function of the irradiation time, at room temperature and in the media under study. For both pesticides, the curves of PIF intensity vs. irradiation time ( $t_{\text{irr}}$ ) were characterized by a regular increase of PIF intensity, which reached a maximum at the optimum irradiation time ( $t_{\text{irr}}^{\text{opt}}$ ) value, followed by a progressive decrease of PIF signal, except for DFB for which the curves leveled off in water/methanol 30/70, v/v and pH 4 water/methanol 30/70, v/v mixtures, at irradiation times larger than about 30 min (Fig. 5). The  $t_{\text{irr}}^{\text{opt}}$  values widely varied from 20 to 30 min for DFB, and from 10 to 20 min for FEN, according to the medium (Table 1). The first, increasing part of the curves corresponded to the photochemical formation of fluorescent photoproduct(s), and the second part indicated their progressive degradation into non- or weakly-fluorescent compound(s). We did not investigate the structures of these fluorescent photoproducts, which should be very probably similar to those of some recently-reported fluorescent DFB and FEN metabolites, such as 4-chlorophenylurea, 4-chloroaniline and *N*-methyl-4-chloroaniline, formed in environmental matrices [2, 38].



**Fig. 5** Effect of the UV irradiation time of FEN ( $5 \times 10^{-6}$  M) on fluorescence intensity in: **a** pH 4 aqueous solution; **b** acetonitrile; **c** methanol; **d** ethanol

Finally, for further analytical PIF studies, we selected, as the most suitable media, a pH 4 mixture water/methanol 30/70, v/v for DFB, and an ethanol solution for FEN, since these media gave the highest PIF signal values with relatively short optimum irradiation times (Table 1).

#### Analytical Figures of Merit

In order to evaluate the analytical interest of the PIF method, we established the analytical figures of merit of DFB and FEN in the different media under study, which are reported in Table 1. To validate PIF, we also determined the analytical figures of merit of both pesticides by the UV–VIS absorption spectrophotometric method (Table 1). All spectral measurements were performed in triplicate for each concentration and in each medium.

Linear plots of PIF intensity and absorbance vs. DFB or FEN concentration [ $I=f(c)$  and  $A=f(c)$ ] were obtained by the PIF method and by UV–VIS absorption spectrophotometry, used as a reference method. As can be seen in Table 1, the linear dynamic range (LDR) values were widely spread over more than one to nearly two orders of magnitude, with correlation coefficients ( $r$ ) very close to unity, indicating an excellent linearity of the analytical curves for both methods. The relative standard deviation (RSD) values ranged, respectively, from 1.7 to 5.6 % for the PIF method, and from 0.5 to 5.2 % for UV–VIS absorption spectrophotometry, according to the pesticide and medium under study. These results showed that the reproducibility of PIF measurements was practically as satisfactory as that of UV–VIS absorption spectrophotometry. The limit of detection (LOD) and limit of quantification (LOQ) values were calculated on the basis of an analyte concentration giving a signal-to-noise ratio (S/N) of, respectively, 3 and 10 (IUPAC criterion). With the PIF method, we obtained rather low LOD values, comprised between 9 and 24  $\text{ng mL}^{-1}$  for DFB, and between 1 and 28  $\text{ng mL}^{-1}$  for FEN, according to the medium, while the corresponding limit of quantification (LOQ) values ranged, respectively, from 30 to 80  $\text{ng mL}^{-1}$  for DFB, and from 4 to 95  $\text{ng mL}^{-1}$  for FEN, according to the medium. A LOD value of about 5  $\text{ng mL}^{-1}$  in propanol-2-ol was also reported by Coly and Aaron [25] for the PIF determination of DFB in technical formulations, in a combined study with other aromatic insecticides. As expected, the LOD and LOQ values obtained by UV–VIS absorption spectrophotometry were largely higher than those determined by the PIF method (Table 1). This confirmed that PIF was much more sensitive than UV–VIS absorption spectrophotometry, and, that PIF was the analytical method of choice for the determination of residues of both pesticides in the environment. Therefore, the validation of PIF by UV–VIS absorption spectrophotometry could be considered as satisfactory.

In addition, it is worthwhile to note that the lowest LOD and LOQ values were obtained by the PIF method in pH 4 mixture water/methanol 30/70, v/v for DFB, and, in ethanol solution for FEN, which again justifies the above-mentioned selection of these media for further PIF analytical studies of both pesticides.

### Analytical Applications

We evaluated the application of the PIF method to the quantitative analysis of tap water and different natural water samples collected in an agricultural area of Senegal. We also attempted to validate the analytical application of PIF by utilizing the UV–VIS absorption spectrophotometric method. All water samples were spiked and analyzed as described in the Experimental Part. We attempted to quantify DFB and FEN in these spiked water samples by means of two approaches, namely the standard addition procedure and the direct spiking procedure with liquid-liquid extraction, using dichloromethane as extracting solvent, in order to eliminate the possible interfering species in natural water samples.

#### Study of Spiked Natural Water Samples

Using the PIF method, we applied the standard addition procedure to tap water and Senegal natural water samples, including river water, draining water, well water, pond water, sea water and rain water, which were spiked either with a DFB standard pH 4 mixture water/methanol 30/70, v/v (concentration = 150 ng mL<sup>-1</sup>), or with a FEN standard ethanol solution (concentration = 25 ng mL<sup>-1</sup>). Then, as mentioned in the Experimental Part, increasing concentrations of DFB and FEN standard solutions were added, and the PIF measurements were performed.

The standard addition curves were linear and the slopes were found to be very close to those measured for the calibration curves, which indicated the absence of significant interference from compounds possibly present in the natural water samples. Satisfactory recovery values were obtained at different concentrations of DFB and FEN for the standard addition procedure as well as for the direct spiking procedure in the PIF method, showing the effectiveness of the extraction procedure. By using the PIF method, the mean recoveries ranged between about 92 and 101 % in tap water, with RSD values of 0.05–8.8 %, and between about 80 and 105 % in natural water samples with RSD values of 0.1–8.0 %, according to the procedure and type of water sample, for both pesticides (Tables 2 and 3). In the case of most water samples, the recovery values were better when using the standard addition procedure than the direct spiking procedure.

Moreover, no significant difference was observed between the recovery values obtained by the PIF method and by UV–VIS absorption spectrophotometry. Indeed, for the latter

reference method, recovery values ranged between 75 and 107 % with RSD values of 0.06–10.4 %, according to the procedure and type of water sample, were found for both pesticides. This demonstrated that the validation of the PIF analytical application, performed by comparing the PIF recovery results with those of the spectrophotometric method, could also be considered as satisfactory. Therefore, taking into account the best sensitivity and selectivity of PIF method compared to classical UV–VIS absorption spectrophotometry, we can conclude that PIF is the method that should be chosen for analytical applications to the determination of DFB and the FEN residues in natural water samples.

#### Interference Studies of Added Foreign Species

The effect on the PIF measurements of foreign species, including four commonly-used pesticides in Senegal, namely fenuron, linuron, pendimethalin and propanil, as well as several inorganic ions (Ca<sup>2+</sup>, (PO<sub>4</sub>)<sub>2</sub><sup>3-</sup>; K<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>, CO<sub>3</sub><sup>-</sup>) likely to exist in the Senegal natural waters, was carried out in order to investigate their possible interference effects on the determination of DFB and FEN. These inorganic ions can be found at relatively small levels in the Senegal natural waters and soils, because of the use of fertilizers and the existence of various chemical industries in the vicinity.

We fixed the concentration of DFB and FEN, and we tested the effect on the pesticide PIF signal of variable concentrations of the interfering species within appropriate ranges (Tables 3 and 4). The tolerance limit of the interfering foreign species was defined as the concentration limit of these interfering species for which the percentage of PIF signal variation did not exceed ± 5 % in the determination of DFB and FEN. For each concentration of interfering species, we calculated, the percentage of variation of the PIF signal, given by the following expression:

$$\Delta F = \frac{F - F_0}{F_0} \times 100$$

with:  $F_0$  = PIF intensity of DFB or FEN alone;  $F$  = PIF intensity of DFB or FEN in the presence of interfering species.

The results concerning the tolerance limit for these foreign species (pesticides and inorganic ions likely to be present with DFB or FEN in Senegal natural waters) are gathered in Table 3 and 4. Using fixed concentrations of, respectively, 0.1 µg mL<sup>-1</sup> for DFB, and 0.015 µg mL<sup>-1</sup> for FEN, we were able to evaluate the interference effects of increasing concentrations of the various, selected foreign species under study (Tables 3 and 4) on the PIF spectra and intensity of DFB and FEN. The concentration intervals of these foreign species were chosen in order to surround the DFB and FEN concentrations.

**Table 2** Analytical application of the PIF method to the determination of FEN, and evaluation of recovery values in spiked tap water and Senegal natural waters obtained by the standard addition and the direct spiking procedures

Type of sample <sup>a</sup>	Added (ng/mL)	Standard addition procedure				Direct spiking procedure				
		Found (ng/mL)	Recovery <sup>b</sup> (%)	Mean Recovery (%)	RSD (%)	Added (ng/mL)	Found (ng/mL)	Recovery <sup>b</sup> (%)	Mean Recovery (%)	RSD (%)
Tap water	0	31.0	–	99.6	0.05	10	9.7	97.0	92.1	8.8
	12.7	43.5	99.6							
	203	233.2	99.7							
	406	435.5	99.6							
	812	840.0	99.6							
River water	0	40.3	–	101.8	0.7	10	11.0	110.0	104.2	7.0
	12.7	53.3	100.6							
	203	248.3	102.0							
	406	456.3	102.2							
	812	872.3	102.3							
Draining water (paddy fields)	0	43.0	–	102.8	1.2	10	9.2	92.0	90.0	2.6
	12.7	56.2	101.0							
	203	253.7	103.1							
	406	464.3	103.4							
	812	885.5	103.6							
Well water	0	28.8	–	101.6	0.5	10	8.3	83.0	86.1	4.3
	12.7	41.8	100.8							
	203	235.8	101.7							
	406	442.8	101.8							
	812	856.8	102.0							
Pond Water	0	38.8	–	98.3	5.0	10	7.8	78.0	83.3	6.2
	12.7	46.8	91.0							
	203	241.2	99.7							
	406	448.6	100.8							
	812	863.3	101.5							
Sea water	0	34.2	–	98.6	0.7	10	8.7	87.0	84.0	4.3
	12.7	46.7	99.6							
	203	233.5	98.4							
	406	432.8	98.3							
	812	831.3	98.2							
Rain water (run off)	0	57.7	–	99.9	0.1	10	10.1	101.0	99.3	2.0
	12.7	70.3	99.8							
	203	260.6	99.9							
	406	463.4	99.9							
	812	869.2	100.0							

RSD relative standard deviation

<sup>a</sup> PIF measurements in ethanol at  $t_{ir}^{opt} = 10$  min

<sup>b</sup> Triplicate measurements for each FEN concentration

We found that the addition of foreign species neither changed the shape of DFB and FEN PIF emission spectra, nor shifted the maximum emission wavelength. But, significant PIF intensity changes occurred with increasing concentrations of foreign species. In the case of the added pesticides, some variations of the PIF signal were noted. Thus, in the case of DFB, an increase of PIF signal was observed upon addition

of linuron, whereas a decrease of PIF intensity was noted for fenuron, fluometuron, monolinuron, diuron, propanil, lindane, and pendimethalin upon increasing concentrations, in the tested concentration range, to the exception of carbaryl, for which a PIF signal increase occurred. In the case of FEN, most interfering pesticides led to a PIF signal enhancement, except for lindane.



**Table 3** Analytical application of the PIF method to the determination of DFB, and evaluation of recovery values in spiked tap water and Senegal natural waters obtained by the standard addition and the direct spiking procedures

Type of sample <sup>a</sup>	Added (ng/mL)	Standard addition procedure				Direct spiking procedure				
		Found (ng/mL)	Recovery (%)	Mean Recovery (%) <sup>b</sup>	RSD (%)	Added (ng/mL)	Found (ng/mL)	Recovery (%)	Mean Recovery (%) <sup>b</sup>	RSD (%)
Tap water	0	188.0	–	101.2	0.8	50	49.7	99.4	99.7	4.9
	50	238.0	100							
	150	341.3	101			100	94.9	94.9		
	300	494.6	101.3							
	600	801.3	101.7			150	157.3	104.8		
	1,200	1414.6	102							
River water	0	217.0	–	100.6	0.3	50	46.0	92.0	93.9	3.0
	50	267.5	100.2							
	150	368.6	100.4			100	97.2	97.2		
	300	520.3	100.6							
	600	823.6	100.8			150	138.7	92.5		
	1,200	1430.3	101							
Draining water (paddy fields)	0	162.0	–	97.4	1.15	50	40.8	81.6	84.5	3.1
	50	210.0	99.0							
	150	305.8	98.0			100	86.8	86.8		
	300	449.3	97.2							
	600	736.4	96.6			150	127.6	85.0		
	1,200	1310.6	96.2							
Well water	0	209.2	–	97.2	1.3	50	43	86.0	83.6	4.4
	50	256.8	99.0							
	150	351.9	97.9			100	79.4	79.4		
	300	494.5	97.1							
	600	779.8	96.4			150	128.3	85.5		
	1,200	1350.5	95.8							
Pond Water	0	122.5	–	105.3	1.9	50	51.9	103.8	104.4	0.5
	50	176.5	102.3							
	150	284.5	104.4			100	104.6	104.6		
	300	446.5	105.7							
	600	770.5	106.6			150	157.2	104.8		
	1,200	1418.6	107.3							
Sea water	0	173	–	105	2.1	50	43.0	86.0	86.7	4.6
	50	227.1	101.8							
	150	335.6	103.9			100	83.0	83.0		
	300	498.2	105.4							
	600	823.6	106.5			150	136.5	91.0		
	1,200	1474.4	107.4							
Rain water (runoff)	0	194.3	–	97.0	1.4	50	36.4	72.8	79.5	8.0
	50	241.7	98.9							
	150	336.5	97.7			100	80.1	80.1		
	300	478.7	96.8							
	600	763.1	96.0			150	128.3	85.5		
	1,200	1332.0	95.5							

RSD relative standard deviation

<sup>a</sup> PIF measurements in pH 4 mixture water/methanol 30/70, v/v at  $t_{ir}^{opt}$  = 30 min

<sup>b</sup> Triplicate measurements for each FEN concentration

The interference effects of various inorganic ions were also investigated, since these species could be present at small

levels in the Senegal natural waters and soils. The occurrence of small amounts of inorganic ions was attributed to the

**Table 4** Interference study of foreign species with DFB<sup>a</sup> and FEN<sup>a</sup>

Foreign species	Interference with DFB		Interference with FEN	
	Tested concentration range (µg/mL)	Tolerance limit <sup>b</sup> (µg/mL)	Tested concentration range (µg/mL)	Tolerance limit <sup>b</sup> (µg/mL)
Pesticide				
Diflubenzuron	–	–	0.0005–0.05	0.01
Fenuron	0.0005–0.5	0.005	–	–
Fluometuron	0.0005–0.2	0.001	0.0010–0.05	0.01
Monolinuron	0.0005–0.5	0.02	0.0005–0.05	0.01
Diuron	0.0001–0.3	0.0005	0.0005–0.05	0.015
Linuron	0.001–0.2	0.02	0.0005–0.05	0.005
Propanil	0.005–0.8	0.03	0.001–0.1	0.01
Pendimethalin	0.0005–0.3	0.03	0.0001–0.02	0.001
Lindane	0.0002–0.3	0.001	0.0001–0.02	0.0005
Carbaryl	0.0005–0.1	0.02	0.005–0.1	0.05
Inorganic ion				
Ca <sup>2+</sup> (PO <sub>4</sub> ) <sub>2</sub> <sup>3-</sup>	0.005–1.0	0.075	0.005–0.1	0.03
K <sup>+</sup> NO <sub>3</sub> <sup>-</sup>	0.01–2.0	0.03	0.003–0.08	0.01
Na <sup>+</sup> CO <sub>3</sub> <sup>-</sup>	0.005–5.0	0.8	0.005–0.3	0.08
Mg <sup>2+</sup> SO <sub>4</sub> <sup>2-</sup>	0.005–0.5	0.075	0.001–0.05	0.01
Fe <sup>3+</sup> SO <sub>4</sub> <sup>2-</sup>	0.005–3.0	0.3	0.003–0.1	0.015

<sup>a</sup> Fixed concentrations=0.1 µg / mL for DFB and 0.015 µg /mL for FEN

<sup>b</sup> See text for definition

geographical position of the studied Senegalese agricultural area close to the Atlantic Ocean, and to the existence of chemical industries in the vicinity. In the case of FEN, a PIF intensity decrease was observed upon adding all inorganic ions in the concentration range under study. In contrast, for DFB, the PIF signal increased upon addition of Na<sub>2</sub>CO<sub>3</sub>, MgSO<sub>4</sub>, FeSO<sub>4</sub> and KNO<sub>3</sub> species, but decreased with Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> increasing concentrations.

The above-described behavior of interfering pesticides and inorganic ions could be due to direct interactions of these species with the DFB photoproduct(s) singlet excited state, producing either a quenching or an enhancement of the PIF signal of DFB or FEN photoproduct(s).

Our results showed that all foreign species under study did produce more or less interference effects on the DFB and FEN PIF signal, depending on their nature and concentration. In the case of pesticides, the highest interference effect on the DFB and FEN PIF signals was observed, respectively, for diuron and lindane, with a tolerance limit value of 0.0005 µg mL<sup>-1</sup>, while the lowest interference effect on the DFB and FEN PIF signals was found, respectively, for propanil and pendimethalin (tolerance limit=0.03 µg mL<sup>-1</sup>), and carbaryl (tolerance limit=0.05 µg mL<sup>-1</sup>). For the remaining pesticides under study, intermediate tolerance limit values between 0.005 and 0.02 µg mL<sup>-1</sup> were obtained (Tables 3 and 4). This suggests that the presence of small concentrations of the tested pesticides, about 0.05 to 0.2 lower than that of DFB and about 0.3 to 0.2 lower than that of FEN, could lead to interferences in the DFB and FEN determination under these conditions.

The inorganic ions under study also produced some notable interference effects on the DFB and FEN PIF signals, since the tolerance limits ranged between 0.03 and 0.8 µg mL<sup>-1</sup> in the case of DFB and between 0.01 and 0.08 µg mL<sup>-1</sup> for FEN, according to the type of inorganic species (Tables 3 and 4). These tolerance limit values corresponded to concentrations about eight times lower to three times higher than that of DFB, and five times lower to two times higher than that of FEN.

Clearly, the existence of all these rather high interference effects yielded by the presence of relatively small levels of either pesticide or inorganic ions in the environment, would require a significant improvement of PIF selectivity for the application of our method to the determination of DFB and FEN in natural water samples, possibly containing these interfering pesticides or inorganic ions. In order to considerably reduce the impact of these interference effects and to improve the PIF selectivity, we feel that it would be possible to use more elaborated spectral methods, including derivative fluorescence (PIF) spectrometry, synchronous fluorescence (PIF) spectrometry, and chemometric techniques combined with PIF, as reported in our previous papers [35, 39, 40].

## Conclusion

We have developed in this work a simple, inexpensive, sensitive and precise PIF method for the determination of two benzoyl- and phenylurea pesticides, namely diflubenzuron

and fenuron, in Senegal natural water samples. We have demonstrated the analytical usefulness of PIF, which was optimized in a pH 4 water/methanol 30/70, v/v mixture in the case of DFB, and in ethanol for FEN. The analytical figures of merit have confirmed the good sensitivity and precision of PIF for both pesticides. We have also shown the applicability of the PIF method to the determination of DFB and FEN residues in fortified natural water samples at the ng mL<sup>-1</sup> level, with satisfactory recovery values. Moreover, PIF was satisfactorily validated by means of UV–VIS absorption spectrophotometry, used as a reference method. Therefore, the results of this study indicate the analytical interest of the PIF method for quantitative analysis of benzoyl- and phenylurea pesticides in environmental water samples. Work is now in progress in our laboratories to combine the PIF detection with a flow injection system, in order to enhance the speed of analysis for routine determination of these pesticides residues in natural water samples.

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