SUPPLEMENTARY INFORMATION

Photochemical Degradation of Marbofloxacin and Enrofloxacin in Natural Waters

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(9 pages)

Reagents and Materials.

MAR and ENR were supplied by Fluka (Sigma-Aldrich), acetonitrile (ACN) by VWR, H_3PO_4 (85% w/w) by Carlo Erba and ultra-pure water from a Millipore Milli-*Q* system. Humic acid sodium salt (MW=100,000-150,000, Aldrich) was used to quantify aquatic humic acids (HAs, see *31*). FQs stock solutions of 300 μg mL^{-1} in methanol 0.1% v/v NaOH 1 M were prepared under red light and stored at 4 °C for <3 months. Working solutions of 30 μg mL^{-1} in 25 mM H_3PO_4 were stored at 4 °C and renewed weekly.

$CaSO_4$ (99%, Sigma-Aldrich), NaCl (100.1%, J.T. Baker), $MgNO_3$ hexaidrate (97%, Sigma-Aldrich), K_2HPO_4 (≥ 99.0%, Sigma-Aldrich) and KH_2PO_4 (99.5%, Merck) salts were used. Ultra-pure HCl acid (37% w/w) and NaOH 0.1 M solution prepared from NaOH anhydrous pellets (97%, Carlo Erba) were employed for pH correction.

Details of Analytical Determination.

The HPLC system consisted of a pump Series 200 (Perkin Elmer) equipped with vacuum degasser, programmable fluorescence detector (FD) and diode array detector (UV) Series 200 (Perkin Elmer). The FD excitation/emission wavelengths selected were 297/507 nm for MAR and 280/450 nm for ENR. After an equilibration period of 5 min, 50 μL of each sample were injected into a 250 × 4.6 mm, 5 μm Ascentis RP-Amide (Supelco) coupled with a similar guard-column. The mobile phase was 25 mM H_3PO_4-ACN (85:15) at a flow rate of 1 mL min^{-1}.

Preparative HPLC experiments were performed with the same HPLC system on a 250 x 10 mm, 5 μm Inertsil ODS-2 (GL Sciences Inc.) preceded by a similar guard-column. Mobile phase was H_2O (pH adjusted to 2.5 with HCl)-ACN (90:10) at a flow rate of 4 mL min^{-1}.

LC-MS analysis was performed by using an Agilent 1100 HPLC with a Gemini C18 (250 x 4.6 mm, 5 μm) column, maintained at 30 °C. A gradient was used for the mobile phase (solvent A: formic acid

0.5% v/v in ultra-pure water; solvent B: ACN) as follows: 15% B until 10 min, 20 % B from 10 to 12 min and 0% B until 1 min, 60% B from 1 to 50 min, for ENR and MAR, respectively. The flow rate was 1.2 mL min^{-1} and the injection volume was 5 μL. The MS-system consisted of a linear trap Thermo LXQ.

A DX 500 Dionex Ion Chromatograph equipped with a GP40 gradient pump, CD20 conductivity detector and anion self-regenerating suppressor (ASRS 400, 4 mm) has been used for the determination of anions content in tap, ditch and river water. 70 μL of each sample were injected into a 250 x 4 mm IonPac AS23 coupled with a AG23 50 x 4 mm guard-column. The eluent was 0.8 mM $NaHCO_3$-4.5 mM Na_2CO_3 at a flow rate of 1 mL min^{-1}.

A Perkin Elmer ICP-OES Optima 3300 DV was used for calcium and magnesium determination, following the operating conditions suggested by the manufacturer.

The pH was monitored with a combined Orion glass electrode 9102 SC, standardized in H^+ activity.

^{1}H-NMR, ^{13}C-NMR and ^{13}C-DEPT spectra were acquired on a Bruker Avance 300 MHz spectrometer and the chemical shifts are reported relative to TMS.

Table S3. Ions Concentrations Determined in Tap and River Ticino

Ion	Concentration (mg L^{-1})	
	Tap water	River Ticino water
Calcium	35.0	37.0
Magnesium	10.0	7.6
Chloride	4.8	10.5
Phosphate	< 0.2	< 0.2
Nitrate	0.6	8.5
Sulphate	4.4	33.2

Table S1. Mass Spectroscopic Data of the Photoproducts of ENR

Fragment	HPLC/ESI-MS/MS											
	comp. D		comp. C		comp. A		comp. B		comp. E		ENR	
	m/e	int.[a]	m/e	int.	m/e	int.	m/e	int.	m/e	int.	m/e	int.
$[M+1]^+$	358.2	10	316.3	80	342.3	15	334.3	25	374.2	100	360.3	10
$[M+1-HF]^+$	-	-	-	-	-	-	314.3	10	-	-		
$[M+1-H_2O]^+$	340.3	5	298.3	20	324.3	5	-	-	356.3	70		
$[M+1-CO_2]^+$	314.3	100	-	-	298.3	100	-	-	-	-	316.3	100
$[M+1-C_2H_7N]^+$	-	-	271.2	25	-	-	289.2	10	-	-		
$[M+1-C_4H_9N]^+$	-	-	245.2	100	-	-	263.2	100	-	-		
$[M+1-C_5H_9NO_2]^+$	-	-	-	-	-	-	219.2	15	-	-		

[a] Relative percent.

Table S4. ^{1}H-NMR Signals of ENR Photodegradation Product D in DMSO-d6

Signal		^{1}H-NMR comp. D	Signal		^{1}H-NMR comp. D
H_A	n.p.	3	H_G	n.p.	1
	δ [ppm]	1.2		δ [ppm]	8.6
	M	m		m	s
H_B, $H_{C,C'}$	n.p.	6	H_H	n.p.	1
	δ [ppm]	3.1-3.2		δ [ppm]	3.8
	M	m		m	m
$H_{D,D'}$	n.p.	4	H_I, H_J	n.p.	4
	δ [ppm]	3.6		δ [ppm]	1.3
	M	bs		m	m
H_E	n.p.	1	H_K	n.p.	1
	δ [ppm]	7.7		δ [ppm]	10.8
	M	s		m	s
H_F	n.p.	1	H_L	n.p.	1
	δ [ppm]	7.5		δ [ppm]	10.5
	M	s		m	bs

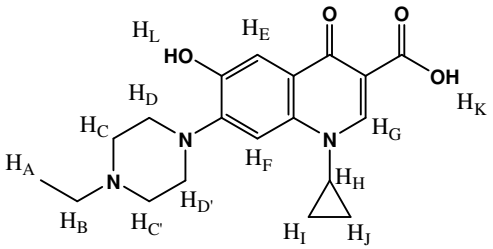

Table S5. ^{13}C-NMR Signals of ENR Photodegradation Product D in DMSO-d6

Signal		^{13}C-NMR comp. D	Signal		^{13}C-NMR comp. D
C_1	c.t.	C	C_{10}	c.t.	C
	δ [ppm]	135.9		δ [ppm]	176.1
C_2	c.t.	C	C_{13}	c.t.	C
	δ [ppm]	148.9		δ [ppm]	35.7
C_3	c.t.	CH	C_{14-15}	c.t.	2xCH_2
	δ [ppm]	105.7		δ [ppm]	7.5
C_4	c.t.	C	C_{17-21}	c.t.	2xCH_2
	δ [ppm]	144.8		δ [ppm]	50.7
C_5	c.t.	C	C_{18-20}	c.t.	2xCH_2
	δ [ppm]	120.2		δ [ppm]	50.2
C_6	c.t.	CH	C_{22}	c.t.	CH_2
	δ [ppm]	108.6		δ [ppm]	46.0
C_8	c.t.	CH	C_{23}	c.t.	CH_3
	δ [ppm]	146.0		δ [ppm]	8.9
C_9	c.t.	C	C_{24}	c.t.	C
	δ [ppm]	106.2		δ [ppm]	166.4

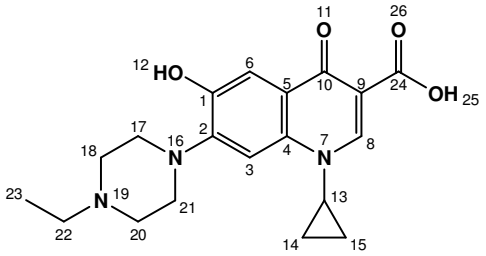

Table S2. Mass Spectroscopic Data of the Photoproducts of MAR

Fragment	HPLC/ESI-MS/MS					
	comp. A		comp. B		MAR	
	m/e	int.[a]	m/e	int.	m/e	int.
$[M+1]^+$	641.5	1	322.3	5	363.1	100
$[M+1-H_2O]^+$	623.4	100	304.3	75		
$[M+1-CO_2]^+$	-	-	278.3	100		
$[M+1-C_4H_7NO_2]^+$	-	-	221.2			

[a] Relative percent.

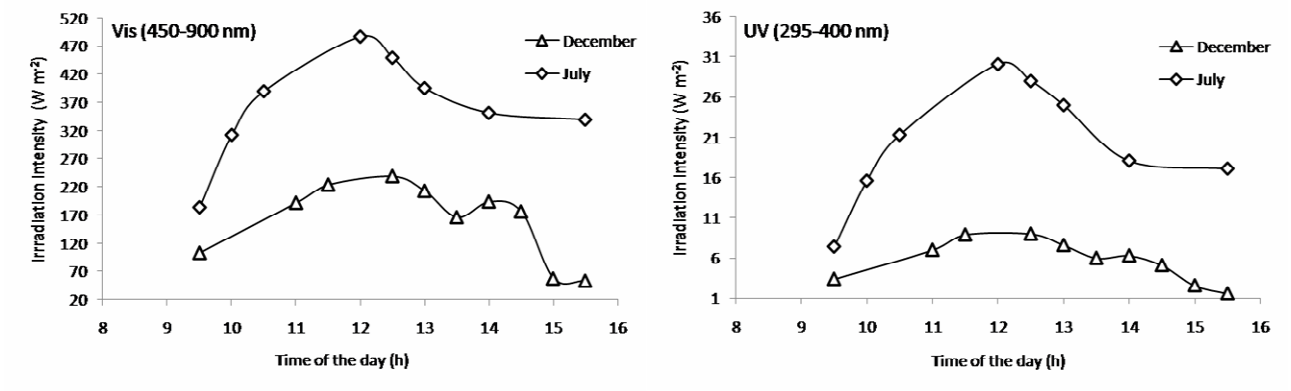

FIGURE S1. Irradiation intensity (W m^{-2}) measured in two different seasons under natural sunlight conditions.

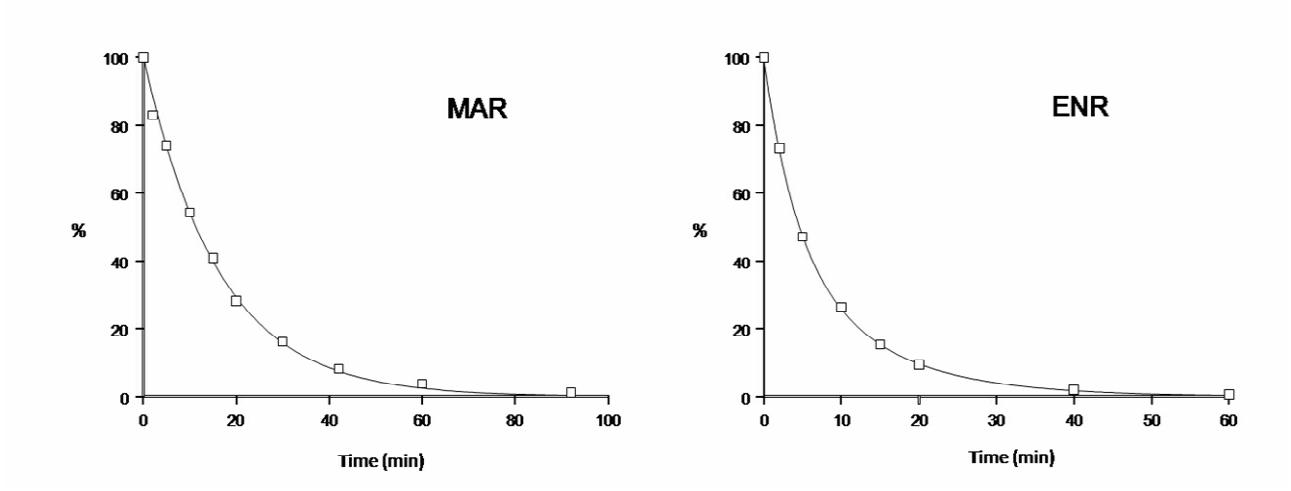

FIGURE S3. Photodegradation profiles obtained by solar-simulated irradiation of MAR and ENR in tap water samples (500 mL, pH 7.9) enriched with 50 μg L^{-1} of either FQs.

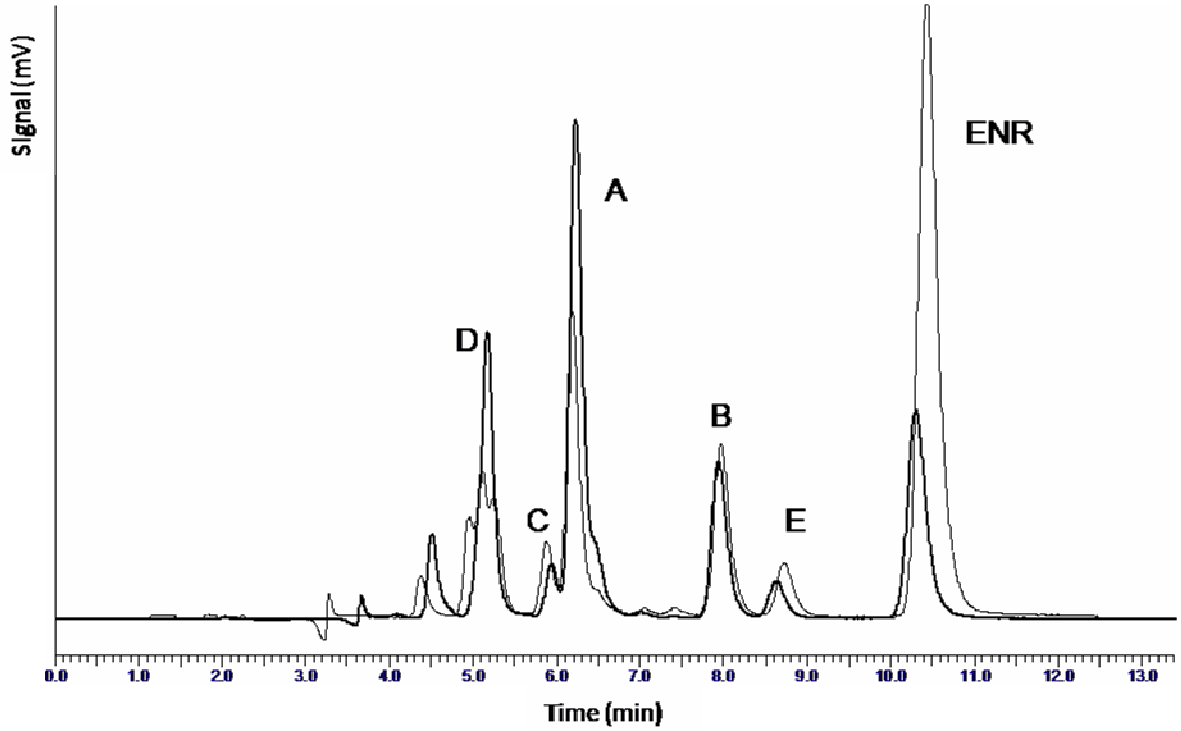

FIGURE S2. FD chromatograms obtained by irradiation of a tap water sample enriched with 50 μg L^{-1} of ENR under natural solar light for 15 min (bold line) and under mercury lamp light (315 nm, 200 W) for 10 min (thin line).