SUPPLEMENTARY INFORMATION

Photodegradation of emerging contaminants in a sunlit wastewater lagoon, seasonal measurements, environmental impacts and modelling

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Quantum yield calculation

Actinometry experiments were conducted using the p-nitroanisole/pyridine (PNA/PYR) actinometer system which has a known, controllable quantum yield, according to the method developed by Dulin and Mill (1982). As noted in method, the quantum yield of PNA was calculated based on the concentration of PYR as: ΦPNA = 0.44 [PYR] + 0.00028 (Dulin and Mill 1982). A concentration of 0.0079 mM for PNA was adopted and appropriate volume of PYR was added into the solution to reach a concentration of 3.2 mM (PYR). The quantum yield of PNA was then calculated to be 0.001688.

This actinometry system was exposed to a solar simulator equip with a Xenon lamp (Abet, Model 11018, USA) and the degradation rates were obtained. Calculation of quantum yield was adapted from the procedures described by Andreozzi et al. (2003). The decay of the concentrations of both the investigated ECs and PNA follow pseudo first-order kinetics. The results for a single photolytic run are reported as a linear relationship:

$$\frac{kEC}{kPNA} = \frac{ln([EC]t/[EC]0)}{ln([PNA]t[PNA]0}$$

Equation 1

For a fixed light source, the measured rate constants, k_{EC} and k_{PNA}, depend on the reaction quantum yields (φ_{ES} and φ_{PNA}) and molar absorptivities of the ECs and of PNA:

$$k_{EC} = \varphi_{EC} \times \sum_\lambda (\varepsilon_\lambda \times f_{p,\lambda})_{EC} \qquad \text{Equation 2}$$

$$k_{PNA} = \varphi_{PNA} \times \sum_\lambda (\varepsilon_\lambda \times f_{p,\lambda})_{PNA} \qquad \text{Equation 3}$$

Where: $f_{p,\lambda}$ (μmol cm^{-2} s^{-1}) is the spectral data (over wavelength interval centred at wavelength λ) for the lamp emission produced by the solar simulator, based on a spectroradiometric measurement (using Ocean Optics USB4000 Spectrometer). $\varepsilon_{\lambda,EC}$ and $\varepsilon_{\lambda,\ PNA}$ (L mol^{-1} cm^{-1}) are the molar absorption coefficients of PNA and the target EC at the wavelength λ, determined using a spectrophotometer. Rearranging Equations 2-3 will result in Equation 4:

$$\frac{kEC}{kPNA} = \frac{\varphi EC \times \sum\lambda(\varepsilon\lambda L\lambda)EC}{\varphi PNA \times \sum\lambda(\varepsilon\lambda L\lambda)PNA} \qquad \text{Equation 4}$$

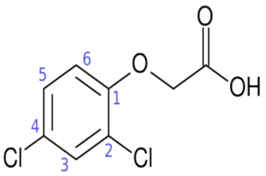
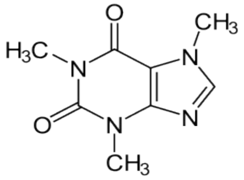
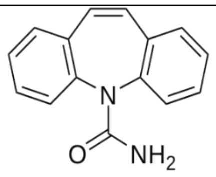
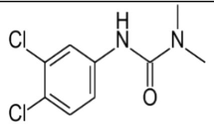
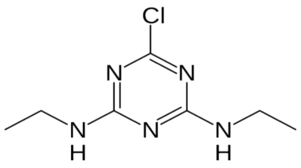
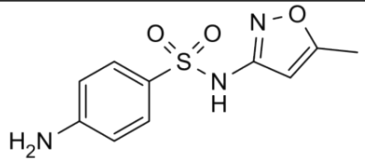
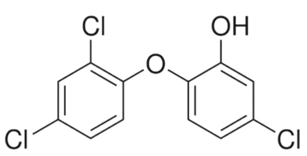
Rearranging Equation 4, The quantum yields for the target ECs can be derived:

$$\varphi_{EC} = \frac{kEC}{kPNA} \times \frac{\sum\lambda(\varepsilon\lambda L\lambda)PNA \times \varphi PNA}{\sum\lambda(\varepsilon\lambda L\lambda)EC} \qquad \text{Equation 5}$$

With a known quantum yield of PNA, the quantum yield of the ECs can then be calculated.

ECs used

Table S1 Structures, CAS number and classification of ECs

Name	2,4-D	Caffeine	Carbamazepine	Diuron
Structure				
CAS	94-75-7	58-08-2	298-46-4	330-54-1
Classification	herbicide	pharmaceutical/anthropogenic marker	anticonvulsant	herbicide
Name	Simazine	Sulfamethoxazole	Triclosan	
Structure				
CAS	122-34-9	723-46-6	3380-34-5	
Classification	triazine herbicide	antibiotic	bactericide	

Solid phase extraction conditions

Solid phase extraction of the target compounds was performed using Oasis HLB cartridges (60 mg, 3 cc, hydrophilic lipophilic balance resin) purchased from Waters Inc. (Australia). The SPE cartridges were initially conditioned using 3 mL HPLC grade methanol followed by 3 mL Milli-Q water. The samples to be analysed were then loaded onto the cartridges which were then vacuum dried for 30 min and then the ECs were eluted with acetonitrile or methanol. Elution conditions and solvents used for the different compounds are summarised in Table S2.

Table S2 Solid phase extraction conditions, elution solvents and recovery study results for ECs

Compound	Conditions	Elution solvent	Recovery (%)
Simazine	-	50:50 Acetonitrile: Methanol	94.8 ± 3.1
Diuron	-	Acetonitrile	95.2 ± 2.2

Carbamazepine	-	50:50 Acetonitrile: Methanol	94.8 ± 3.1
2,4-D	pH 2.8	Acetonitrile	95.3 ± 1.2
Caffeine	-	Acetonitrile	96.8 ± 2.3
Sulfamethoxazole		50:50 Acetonitrile: Methanol	95.7 ± 2.1
Triclosan	pH 5.0	Acetonitrile	96.1 ± 1.4

High performance liquid chromatography conditions

Sample (20 µL) was directly injected into the HPLC fitted with an Agilent Poroshell C18 reverse-phase chromatography column (100 x 2.7 mm, particle size 1.8 µm). ACN = acetonitrile.

Table S3 Summary of the HPLC parameters for ECs and actinometer (flow rate = 0.5 mL min^{-1})

Compound	**Ratio of mobile phases**	**Detection wavelength (nm)**	**Retention time (min)**
Simazine	H_2O : ACN (50 : 50)	270	3.5
Diuron	H_2O : ACN (45 : 55)	254	3.8
Carbamazepine	H_2O : ACN (35 : 65)	286	2.5
2,4-D	Phosphate buffer (pH=2.8) : ACN (50 : 50)	250	4.0
Caffeine	H_2O : MeOH (60 : 40)	273	4.5
Sulfamethoxazole	H_2O : ACN (35 : 65)	237	3.5
Triclosan	H_2O : ACN (25 : 75)	280	2.2
PNA	Phosphate buffer (pH=2.8) : ACN (50 : 50)	310	3.8

References

Andreozzi, R., Raffaele, M. and Nicklas, P. (2003) Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. Chemosphere 50(10), 1319-1330.

Dulin, D. and Mill, T. (1982) Development and evaluation of sunlight actinometers. Environmental science & technology 16(11), 815-820.