Xenobiotics removal by phototransformation in the context of tertiary treatment

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INTRODUCTION

Wastewater treatment plants (WWTP) have been singled out as one of the main point-sources of xenobiotics (pesticides and pharmaceutically-active compounds) transfer into the aquatic environment. Indeed, biological secondary WWTPs partially eliminate xenobiotics present in domestic and industrial discharges and release significant concentrations of several xenobiotics, due to their poor biodegradation in secondary treatments and/or their high levels in raw influents (Soulier et al., 2011).

Tertiary treatments can be set up in order to ensure a better elimination of xenobiotics in effluents from secondary treatment.

In fact, phototransformation (figure 1) is an elimination process that could be used in tertiary treatment, such as planted discharge area or polishing ponds. This elimination follows a first order kinetics :

$$-\frac{d[S]}{dt} = k.[S] \qquad \rightarrow t1/2 = \frac{\ln 2}{k}$$

where [S] is the concentration of xenobiotics, k is the rate constant of photolysis and $t_{1/2}$ is the half-life of xenobiotics.

Objective:
- **Evaluate the effectiveness of direct and indirect phototransformation of selected xenobiotics in tertiary treatment and determine the influence of physico-chemical parameters of the aquatic environment**

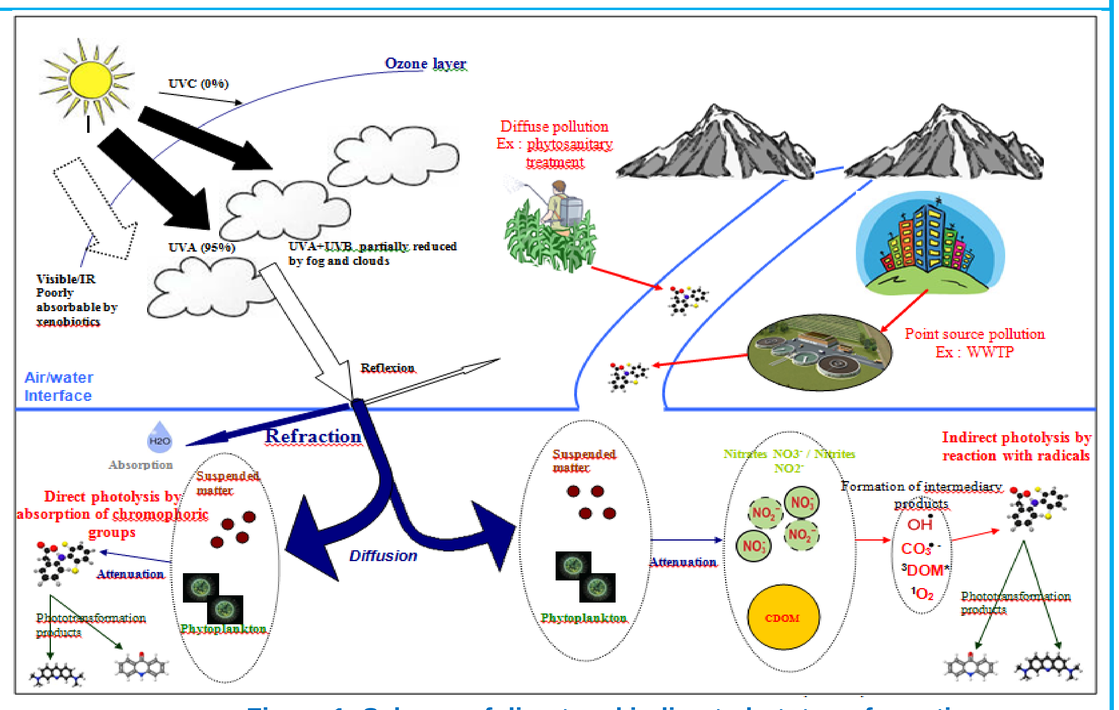

Figure 1: Schema of direct and indirect phototransformation

METHODS

We have created a **database** using data from **70 papers** published between 1977 and 2013. It contains **349 data lines** in an Excel spreadsheet (table 1) with at least one of the following descriptor of xenobiotics phototransformation: removal efficiency, kinetic rate constant of direct and indirect photolysis and half-life. We also compiled information on the operating conditions and the chemical structure of the compound and their phototransformation products.

We have focused our study on several xenobiotics known to be **poorly biodegradable, poorly adsorbable** and **frequently** found in effluents of secondary treatment.
A total of **13 substances** were selected: erythromycin and roxithromycin (antibiotics), carbamazepine (antiepileptic), diazepam (benzodiazepine), diclofenac (anti-inflammatory drug), metoprolol, timolol, propranolol, atenolol and sotalol (beta-blockers), simazine, diuron and isoproturon (pesticides).

Table 1: Example of one line in the phototransformation database

Reference	Xenobiotic	Chemical structure	Family	Chromophoric groups: Azo (-N=N-)	Nitroso (-N=O ou -N-OH)	Carbonyle (>C=O)	Vinyl (-C=C-)	Nitro (-NO2 ou =NO-OH)	Thiocarbonyle (>C=S)	Methine (-CR=)	Azomethine (-CH=NH)	Azomethine N substitué (-CH=N-)	Azoxy (-N=NO-)	Indice de phototransformation IP	Type of Photodegradation	Initial concentration (µg/L)	Type of water	Characteristics of the radiation: Type of radiation	geographical position	Radiation intensity (J.m-2)	Light flow(J.m-2.s-1)	Power (W)	λsource (nm)	Date of experiment	Description of the experimental environment	Depth (m)	Temperature: Min (°C)	Max (°C)	Exposure time (min)	Concentration of reagents	Nitrate concentration (mg/L)	TOC concentration (mg/L)	DOC concentration (mg/L)	DOM concentration (mgC/L)	Humic acid concentration (mg/L)	Removal efficiency (%): Valeur	Incertitude (±)	Quantum yield Φ: Valeur	Incertitude (±)	k (h-1): Valeur	Incertitude (±)	t1/2 (h): Valeur	Incertitude (±)	Observation	Analytical method	LQ/LD	Phototransformation products	Observation Phototransformation products
(Lam and Mabury 2005)	Carbamazepine		Antiepileptic	0	0	1	7	0	0	0	0	0	0	8	Simulated	#N/A	Surface water	Xenon lamp	#N/A	#N/A	765	#N/A	>290	#N/A	Quartz tube V=10mL	#N/A	27	27	#N/A	[HCO3-]=0.8 mM	49.6	#N/A	#N/A	0,7	#N/A	#N/A	#N/A	#N/A	#N/A	0,012603	#N/A	55	3	#N/A	LC-MS/MS	#N/A	10,11-epoxycarbamazepine	#N/A

RESULTS

Phototransformation efficiency

We have sorted arbitrarily xenobiotics in 3 classes according to their capacities of transformation under direct photolysis (table 2): Fast (++), medium (+) and low (-) phototransformable. This classification in 3 classes is useful because it estimates if phototransformation can be expected as an effective way to remove xenobiotics in WWTP process. For example, for a polishing ponds having residence times of 20 days, the removal efficiencies would be 100% for diclofenac, 47% for diuron and 12% for carbamazepine.

The comparison of half-lives of direct and indirect photolysis allowed us to put forward various scenarios that may be encountered:
- No significant differences between direct and indirect photolysis (timolol and diclofenac)
- Presence of nitrates favored the transformation of xenobiotics (propranolol, diuron, atenolol, carbamazepine, metoprolol)
- The presence of DOM and especially humic substances promoting phototransformation (diazepam, propranolol, atenolol, metoprolol)
- In some cases, the presence of DOM had a screening effect and slows phototransformation (simazine, carbamazepine)

Table 2: Half-lives for direct and indirect phototransformation for 13 xenobiotics under solar radiation.

	Half-life (hours) Without NO_3^- and DOM	Grade global score	Half-life (hours) With NO_3^-	Half-life (hours) With DOM	Grade global score
Simazine	0.08 [0.03 ; 0.13] (n=3)	++	1392 [696 ; 2424] (n=3)	1392 [696 ; 2424] (n=3)	-
Isoproturon	2.5 [1.4 ; 5] (n=4)	++	N.I.A	N.I.A	N.I.A
Timolol	4.3 (n=1)	++	N.I.A	2.6 [0.6 ; 4.6] (n=4)	++
Diclofenac	4.9 [0.005 ; 47] (n=33)	++	2.0 [0.012 ;5.2] (n=5)	3.7 [0.002 ; 18.4] (n=5)	++
Sotalol	6 (n=1)	++	N.I.A	N.I.A	N.I.A
Diazepam	28 [3 ; 103] (n=5)	+	N.I.A	13 [3 ; 28] (n=4)	++
Propranolol	66 [0.3 ; 408] (n=48)	+	19 [3 ; 37] (n=3)	12 [0.07 ; 27] (n=4)	++
Diuron	521 [4 ; 3192] (n=8)	+	25 [3 ; 84] (n=19)	N.I.A	+
Atenolol	1248 [0.1 ; 3984] (n=13)	-	4.4 [0.05 ; 11.4] (n=10)	4.2 [0.1 ; 10.8] (n=7)	++
Carbamazepine	2625 [17 ; 12600] (n=35)	-	284 [6 ; 1227] (n=16)	1775 [0.06 ; 12154] (n=7)	-
Metoprolol	3572 [29 ; 11632] (n=14)	-	656 [526 ; 786] (n=2)	6.5 [0.2 ; 12.8] (n=4)	+
Erythromycin	N.I.A	N.I.A	N.I.A	N.I.A	N.I.A
Roxithromycin	N.I.A	N.I.A	361 [1.6 ; 720] (n=2)	1.6 (n=1)	+

($t_{1/2}$mean [Min ; Max] (number of data)) ; (++) half-life less than 24 hours; (+) half-life between 24 and 720 hours; (-) half-life greater than 720 hours ; N.I.A = No Information Available.

Phototransformation products

Knowledge on the degradation of the parent compound is only a first step. It is necessary to improve knowledge of the phototransformation products which may be more toxic and / or more persistent than the parent compound (eg, acridine, phototransformation products of carbamazepine; Donner et al., 2013).

That is why 133 phototransformation products were extracted from 28 scientific papers and compiled in a database. This second database was used to develop a method of analysis for the selected degradation products by UPLC-QTOF-MS/MS.

71% of detections of these phototransformation products originatefrom the process of direct photolysis, while indirect photolysis is the most important pathway in natural environment or planted discharge area. Direct and indirect photolysis have different mechanisms of action on the xenobiotics.
Example: The phototransformation of carbamazepine gave the same major products for the two processes (i.e., acridine). However, a minor product differed in each case: acridone was detected under direct photolysis; while dihydroxycarbamazepine was detected under indirect photolysis (Chiron et al., 2006).

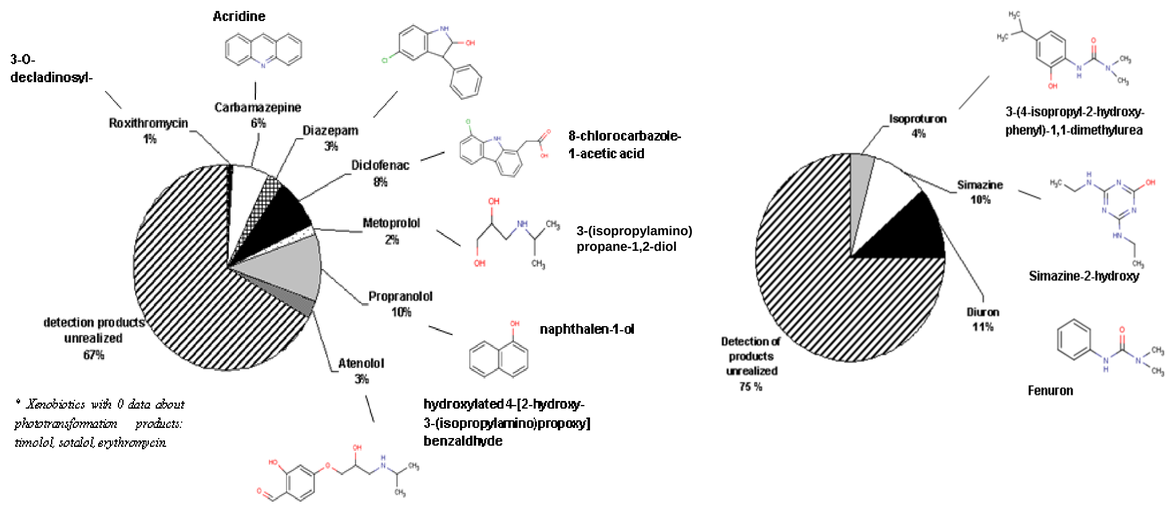

Figure 2: Repartition of collected data on the phototransformation products in our database and representation of the major phototransformation products for the xenobiotics studied, for pharmaceutical (left) and pesticides (right)

CONCLUSIONS

- **3 classes** of xenobiotics were proposed: fast, medium and low phototransformable. This classfication allowed to assess the **effectiveness of a tertiary treatment** type planted discharge area or polishing pond according to its residence time
- From the 13 xenobiotics selected, we also compiled **all phototransformation products** detected in 28 scientific papers in order to develop an analytical method by UPLC-QTOF-MS/MS. This method will be used in future experiments whose aim is to **compare the phototransformation products formed under direct and indirect photolysis**
- Future experiments will be conducted at the **laboratory scale** and in **planted discharge area** in order to **create a model** to simulate the removal of xenobiotics based on physico-chemical of environmental parameters and xenobiotics

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Donner, E. , Kosjek, T., Qualmann, S., Kusk, K.O., Heath, E., Revitt, D.M., Ledin, A,, Andersen, H.R. Ecotoxicity of carbamazepine and its UV photolysis transformation products. *Science of the Total Environment* 443, 870-876 (2013).
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