Supplementary Information for:

Elimination of micropollutants by solar/chlorine process:

Contribution of reactive species and formation risk of NDMA

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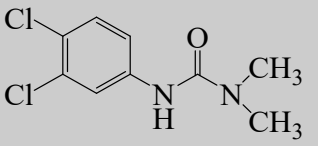
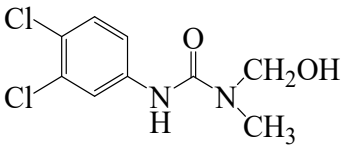
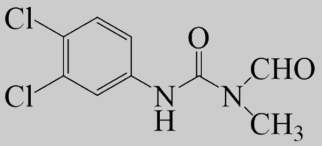
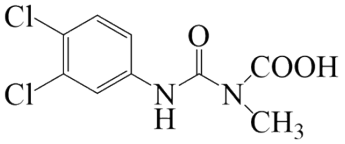
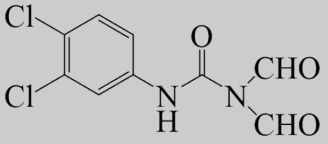
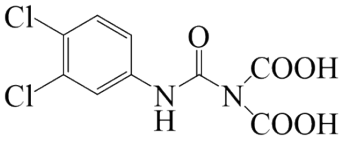
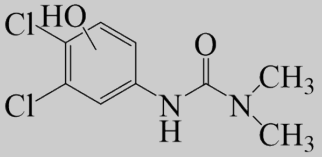
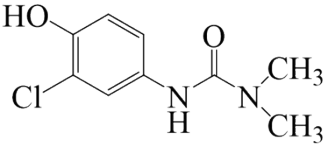
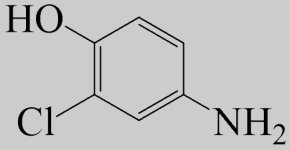
Figure S1. Setup of photochemical reactor.

Table S1 analytical methods.

	Methanol	Ultrapure water	Wavelength(nm)	Injection volume(μL)
Diuron	80%	20%	254	20
NB	70%	30%	263	50

Table S2 HPLC-MS/MS data of possible organic products formed during the diuron degradation at negative mode.

Compound	$[M+H]^+$ (m/z)	Chemical formula	Proposed structure
Diuron	233.0	$C_9H_{10}Cl_2N_2O$	
TP1	249.0	$C_9H_{10}Cl_2N_2O_2$	
TP2	247.0	$C_9H_8Cl_2N_2O_2$	
TP3	263.0	$C_9H_8Cl_2N_2O_3$	
TP4	261.0	$C_9H_6Cl_2N_2O_3$	
TP5	293.0	$C_9H_6Cl_2N_2O_5$	
TP6	250.0	$C_9H_{11}Cl_2N_2O_2$	
TP7	215.1	$C_9H_{11}ClN_2O_2$	
TP8	126.1	C_6H_6ClNO	

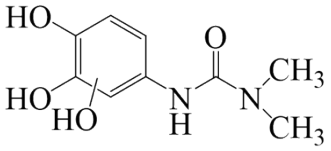
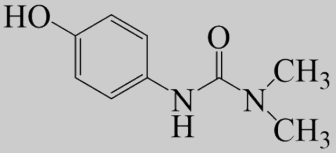
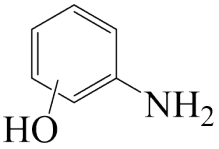
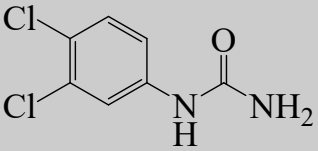
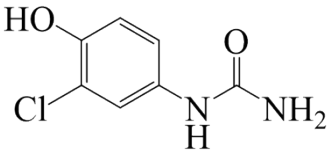
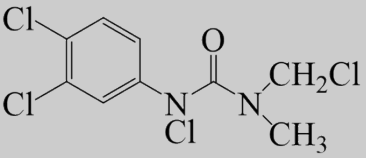
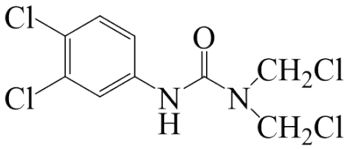
TP9	214.1	$C_9H_{13}N_2O_4$	
TP10	181.1	$C_9H_{12}N_2O_2$	
TP11	111.1	$C_6H_8Cl_2NO$	
TP12	205.0	$C_7H_6Cl_2N_2O$	
TP13	187.0	$C_7H_7ClN_2O_2$	
TP14	300.9	$C_9H_8Cl_4N_2O$	
TP15	300.9	$C_9H_8Cl_4N_2O$	

Table S3 Elemental Compositions of NOM.

	Cat. No.	**H_2O**	**Ash**	**C**	**H**	**O**	**N**	**S**	**P**	**δ^{13} C**	**δ^{15} N**
Suwannee River	2R101 N	5.69	4.01	50.70	3.97	41.48	1.27	1.78	nd	nd	nd

Text S1 Detailed experimental procedures.

Solar exposure was proceeded in a specially designed photochemical reactor (XPA-7, Xujiang Electromechanical Plant, Nan Jing, China) equipped with a 500-W Xenon lamp with daylight filter (cutoff below 290 nm) and infrared radiation filter to generate simulated sunlight. A 1.67 mL volume test solution with diuron (0.15 mM) was prepared in a quartz tube and buffered by 2.5 mM phosphate buffer solution (pH = 6 – 8). Sodium hypochlorite solution was added into the tube to reach a desire concentration of available chlorine (100, 200, 300 μM) and simultaneously exposed to solar irradiation. The temperature was controlled at 25 ± 1 °C. Control experiments of diuron degradation were conducted in a similar procedure by direct dark chlorination and solar irradiation, respectively.

Text S2 Detailed analytical methods.

HPLC (Agilent 1260, USA) equipped with a C18 column (150 mm×4.6 mm×5 μm, Agilent, USA) and a variable wavelength detector (VWD) (Agilent, USA) was used to determine the concentration of diuron. The wavelength of detector was set at 254 nm. The mobile phase was a mixture of methanol and ultrapure water (1‰ formic acid) at a ratio of 80: 20 and the flow rate at 1.0 mL min^{-1}.

HPLC-MS/MS (Agilent 1290/6460 Triple Quad) equipped with a Symmetry C18 column (50 mm × 2.1 mm × 5 mm, Agilent, USA) in positive electrospray ionization (ESI) mode was used to identified NMDA and the transformation products of diuron. When detected the transformation products, the mobile phase consisted of ultrapure water as solvent A (1‰ formic acid) and acetonitrile as solvent B at a flow rate of 0.2 mL min^{-1}, with a gradient elution program as follows: 5% to 70% B from 0 to 7 min; 70% to 95% B from 7 to 8 min; 95% to 5% B from 8 to 9 min; 5% B from 9 to 10 min. The injection volume was 5 μL, and column temperature was 25 °C. When quantified the formed NDMA, HPLC-MS/MS was set at positive mode using MRM method by monitoring the product ions of 58.2 and 42.9 m/z. The mobile phase was a mixture of methanol and ultrapure water (1‰ formic acid) at a ratio of 50:50 and the flow rate at 0.2 mL min^{-1}.

The molar yields of NDMA were calculated by dividing the formed NDMA concentrations with the initial diuron concentrations, as shown in the following equation:

$$\text{NDMA yield}(\%)=([\text{NDMA}]/[\text{diuron}]_0) \times 100$$