Article

Enhanced Degradation of Different Tetracyclines by Nonthermal Plasma and Activated Persulfate: Insights into Synergistic Effects and Degradation Mechanism

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Supplementary Information

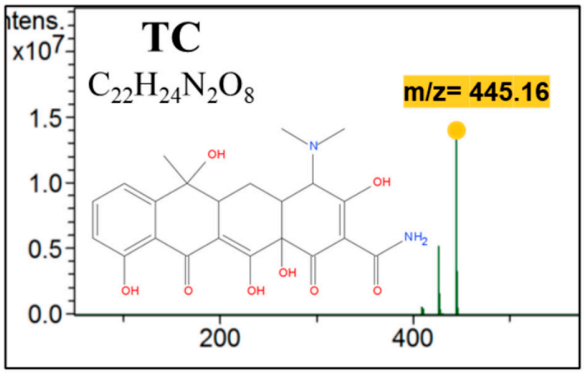
Text S1: Materials:

All chemicals used in this study were of analytical grade and used without further purification. Tetracycline, Oxytetracycline, Chlortetracycline, and Acetonitrile were purchased from Sigma Aldrich. Phosphoric acid and Sodium Persulfate, as PS) were from Samchun, Republic of Korea. Tert-butyl alcohol ($C_4H_{10}O$, as TBA), 1,4-benzoquinone ($C_6H_4O_2$, as BQ), and ethanol were obtained from Daejung Chemical, Republic of Korea. All other reagents were obtained from Samchun Chemical, Republic of Korea.

Text S2:

The contribution of individual reactive species was examined through scavenging experiments using tert-butyl alcohol (TBA, 100 mM) to quench $^{\bullet}OH$, ethanol (EtOH, 100 mM) as a broad-spectrum scavenger for both electrons e- and $SO_4^{\bullet-}$, and para-benzoquinone (BQ, 1 mM) for superoxide radicals ($^{\bullet}O_2^-$). Quenchers were added to the solution two minutes before plasma initiation. The effects of each quencher on TCs degradation were compared to control experiments to infer the dominant reactive species in the plasma and NTP/PS systems.

Degradation byproducts were analyzed using liquid chromatography coupled with mass spectrometry (LC-MS/MS). The system was equipped with an electrospray ionization (ESI) source and a C18 column (50 mm × 2.1 mm, 1.8 μm; Agilent Technologies). To evaluate the potential environmental risks associated with the degradation byproducts, the Toxicity Estimation Software Tool (T.E.S.T., U.S. EPA) was used to estimate the toxicity of each identified intermediate. After proposing the degradation pathway based on LC-MS/MS analysis, the chemical structures of the byproducts were input into T.E.S.T. to predict endpoints.


Intens.
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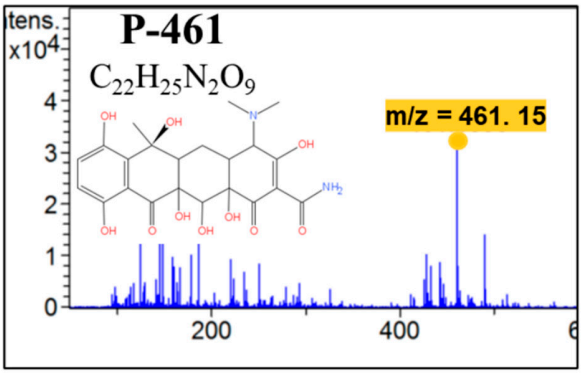
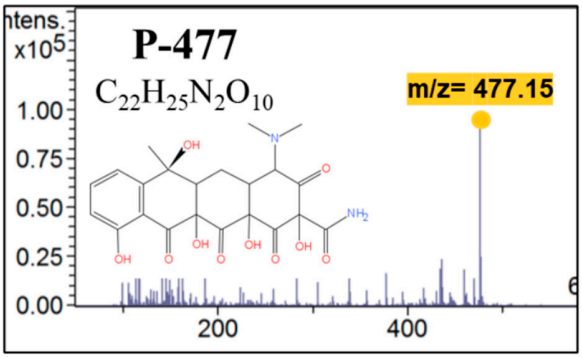
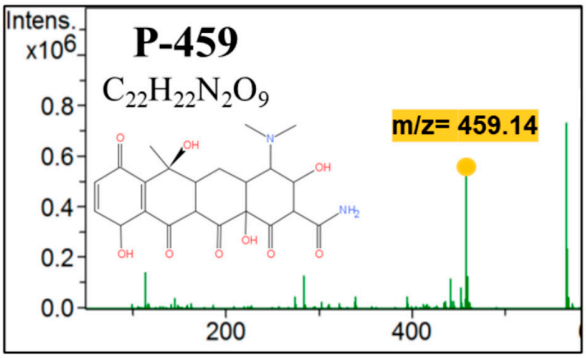
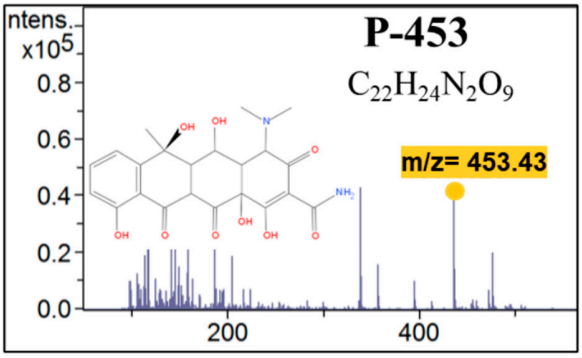
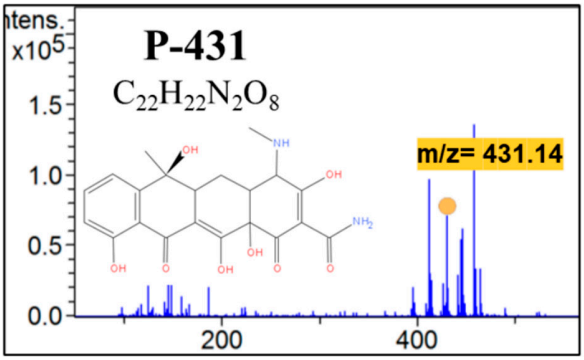
TC
C22H24N2O8
m/z= 445.16
200
400

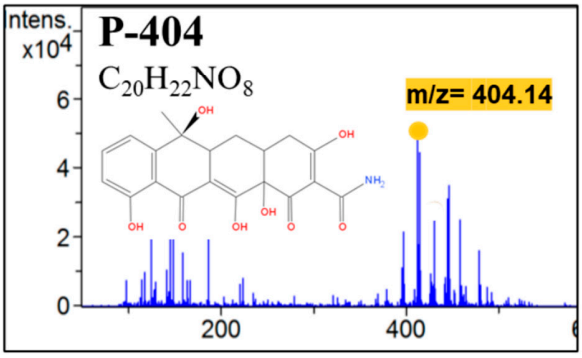

Intens.
x10^4
4
3
2
1
0
P-461
C22H25N2O9
m/z = 461. 15
200
400

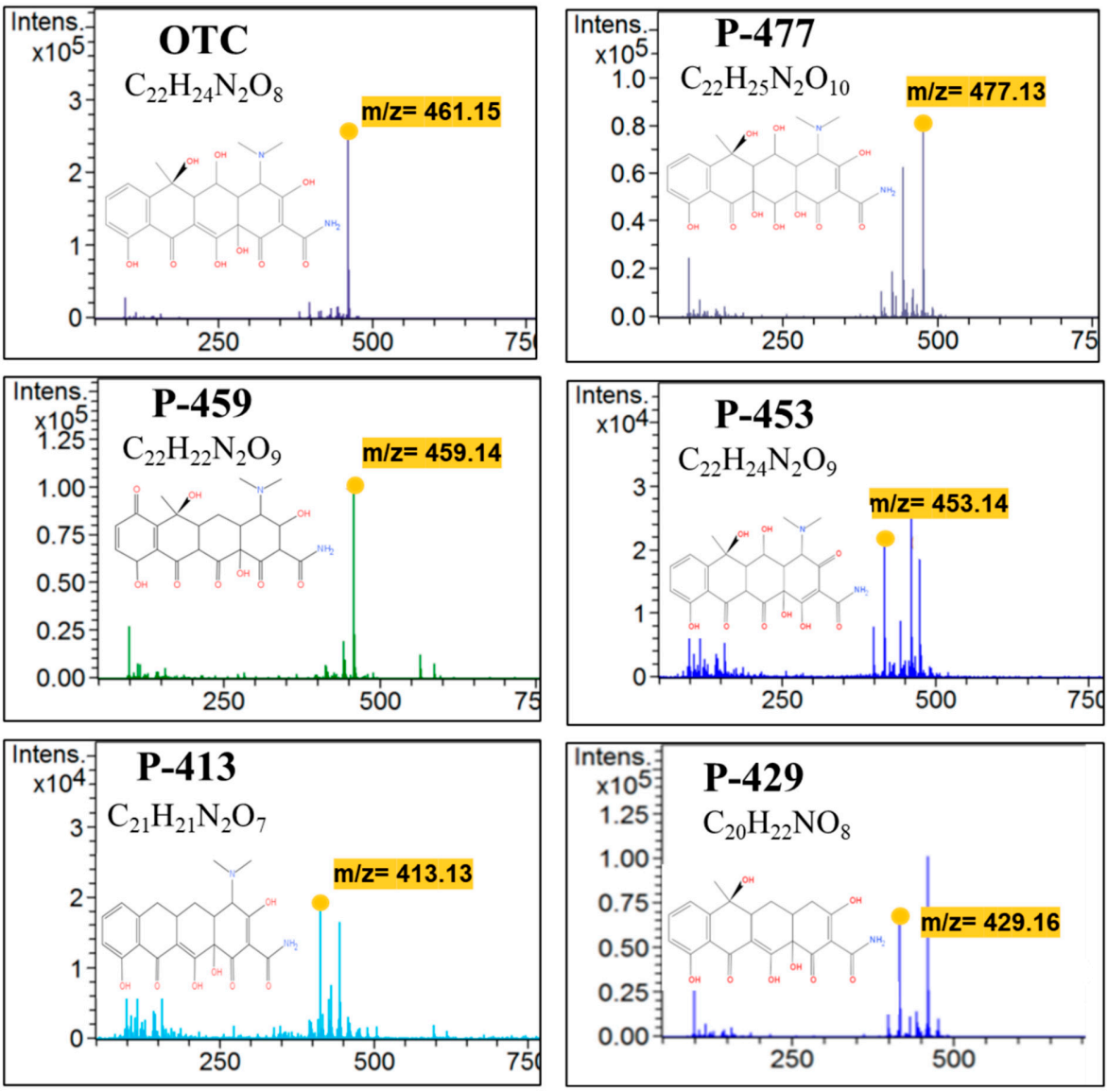

Intens.
x10^5
1.00
0.75
0.50
0.25
0.00
P-477
C22H25N2O10
m/z= 477.15
200
400


Intens.
x10^6
0.8
0.6
0.4
0.2
0.0
P-459
C22H22N2O9
m/z= 459.14
200
400


Intens.
x10^5
0.8
0.6
0.4
0.2
0.0
P-453
C22H24N2O9
m/z= 453.43
200
400


Intens.
x10^5
1.5
1.0
0.5
0.0
P-431
C22H22N2O8
m/z= 431.14
200
400


Intens.
x10^4
6
4
2
0
P-404
C20H22NO8
m/z= 404.14
200
400


OTC
$C_{22}H_{24}N_2O_8$
m/z= 461.15
P-477
$C_{22}H_{25}N_2O_{10}$
m/z= 477.13
P-459
$C_{22}H_{22}N_2O_9$
m/z= 459.14
P-453
$C_{22}H_{24}N_2O_9$
m/z= 453.14
P-413
$C_{21}H_{21}N_2O_7$
m/z= 413.13
P-429
$C_{20}H_{22}NO_8$
m/z= 429.16
Intens.

F

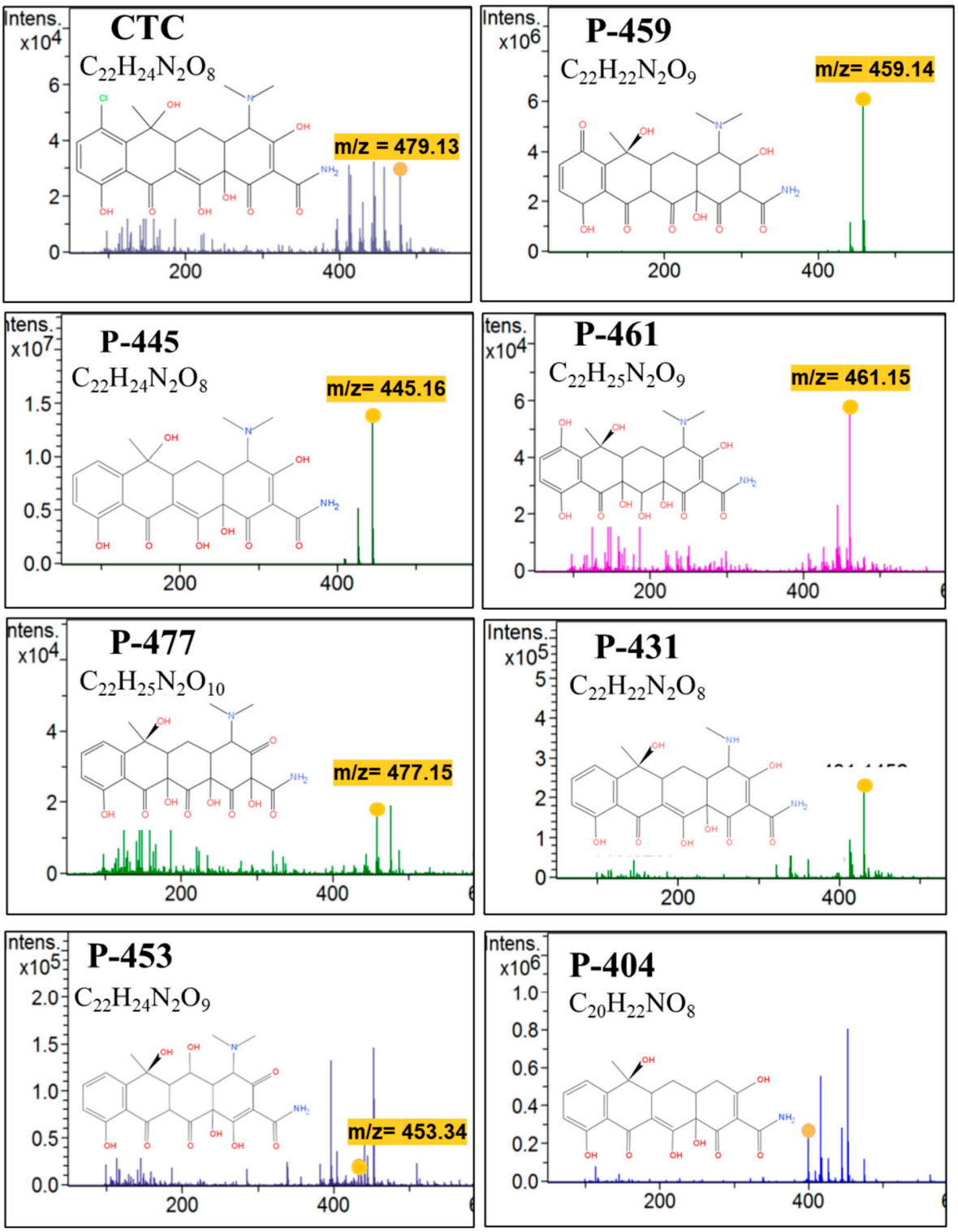


Figure S1: LCMSMS Spectra.

Table S1. Degradation products Toxicities.

Tetracycline (TC) m/z= 445.16 ($C_{22}H_{24}N_2O_8$)	**Oxytetracycline (OTC)** m/z= 461.16 ($C_{22}H_{24}N_2O_8$)
Developmental toxicity: 0.86 Mutagenicity: 0.66 Oral rat LD 50 2.46 -Log10 (mol/kg) Daphnia magna LC50 (48H): 4.41 -Log10 (mol/kg) Bioconcentration factor: 0.71	Developmental toxicity: 0.83 Mutagenicity: 0.56 Oral rat LD 50 2.36 -Log10 (mol/kg) Daphnia magna LC50 (48H): 4.59 -Log10 (mol/kg) Bioconcentration factor: 7.86
Chlortetracycline (CTC) m/z= 445.16 ($C_{22}H_{24}N_2O_8$)	**P-461** m/z= 461.15 ($C_{22}H_{25}N_2O_9$)
Developmental toxicity: 0.86 Mutagenicity: 0.66 Oral rat LD 50 2.46 -Log10 (mol/kg) Daphnia magna LC50 (48H): 4.41 -Log10 (mol/kg) Bioconcentration factor: 0.71	Developmental toxicity: 0.65 Mutagenicity: 0.66 Oral rat LD 50 2.46 -Log10 (mol/kg) Daphnia magna LC50 (48H): 4.41 -Log10 (mol/kg) Bioconcentration factor: 0.71
P-461m/z= 477.15 ($C_{22}H_{25}N_2O_{10}$)	**P-477** m/z= 477.15 ($C_{22}H_{25}N_2O_{10}$)
Developmental toxicity: 0.72 Mutagenicity: 0.61 (Mut +) Oral rat LD 50 2.69 -Log10 (mol/kg) Daphnia magna LC50 (48H): 3.88 -Log10 (mol/kg) Bioconcentration factor: -1.05	Developmental toxicity: 0.86 Mutagenicity: 0.67 (Mut +) Oral rat LD 50 2.46 -Log10 (mol/kg) Daphnia magna LC50 (48H): 4.09 -Log10 (mol/kg) Bioconcentration factor: 0.12
P-459 m/z= 459.14 ($C_{22}H_{22}N_2O_9$)	**P-431**m/z= 431.16 ($C_{22}H_{22}N_2O_8$)
Developmental toxicity: 0.85 Mutagenicity: 0.73 (Mut +) Oral rat LD 50 2.40 -Log10 (mol/kg) Daphnia magna LC50 (48H): 3.12 -Log10 (mol/kg) Bioconcentration factor: 0.18	Developmental toxicity: 0.85 Mutagenicity: 0.65 (Mut +) Oral rat LD 50 2.33 (mol/kg) Daphnia magna LC50 (48H): 4.79 -Log10 (mol/kg) Bioconcentration factor: -0.35
P-429 m/z= 429.14 ($C_{21}H_{22}NO_7$)	**P-453**
Developmental toxicity: 0.82 Mutagenicity: 0.65 (Mut +) Oral rat LD 50 2.43 (mol/kg) Daphnia magna LC50 (48H): 4.9 -Log10 (mol/kg) Bioconcentration factor: 0.11	Developmental toxicity: 0.83 Mutagenicity: 0.64 (Mut +) Oral rat LD 50 2.36 (mol/kg) Daphnia magna LC50 (48H): 4.12 -Log10 (mol/kg) Bioconcentration factor: 0.12
P-163.04 m/z= 163.004 ($C_8H_{12}O_3$)	**P-145** m/z= 145.10 ($C_8H_{15}O_2$)
Developmental toxicity: 0.45 Mutagenicity: (Mut -) 0.09 Oral rat LD 50 (mol/kg) 2.35 Daphnia magna LC50 (48H): -Log10 (mol/kg) 3.5 Bioconcentration factor: 0.14	Developmental toxicity: 0.43 Mutagenicity: (Mut +) 0.15 Oral rat LD 50 (mol/kg) 4.5 Daphnia magna LC50 (48H): 3.92 -Log10 (mol/kg) Bioconcentration factor: 0.27 log10

P-413 $C_{21}H_{21}N_2O_7$	**P-404** $C_{20}H_{22}NO_8$
Developmental toxicity: 0.9 Mutagenicity: (Mut +) 0.6 Oral rat LD 50 -log (mol/kg) 2.50 Daphnia magna LC50 (48H): -Log10 (mol/kg) 5.41 Bioconcentration factor: 0.22	Developmental toxicity: 0.85 Mutagenicity: (Mut +) 0.7 Oral rat LD 50 (mol/kg) 2.59 Daphnia magna LC50 (48H): 4.92 -Log10 (mol/kg) Bioconcentration factor: -0.07
P-114 m/z= 114. $C_6H_{10}O_2$	**P-158** 158 $C_7H_{10}O_4$
Developmental toxicity: 0.74 Mutagenicity: (Mut -) 0.09 Oral rat LD 50 (mol/kg) 1.94 Daphnia magna LC50 (48H): -Log10 (mol/kg) 2.88 Bioconcentration factor: 1.00	Developmental toxicity: 0.51 Mutagenicity: (Mut -) 0.15 Oral rat LD 50 (mol/kg) 2.09 Daphnia magna LC50 (48H): -Log10 (mol/kg) 1.63 Bioconcentration factor: -0.48