Supporting Information

Multiple roles of humic acid in the photolysis of sulfamethoxazole: Kinetics and mechanism

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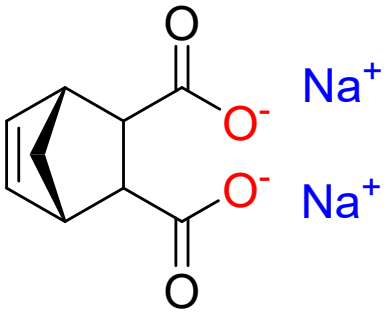


Fig S1 The chemical structure of HA

Fig S2: Diagram of photoreactor

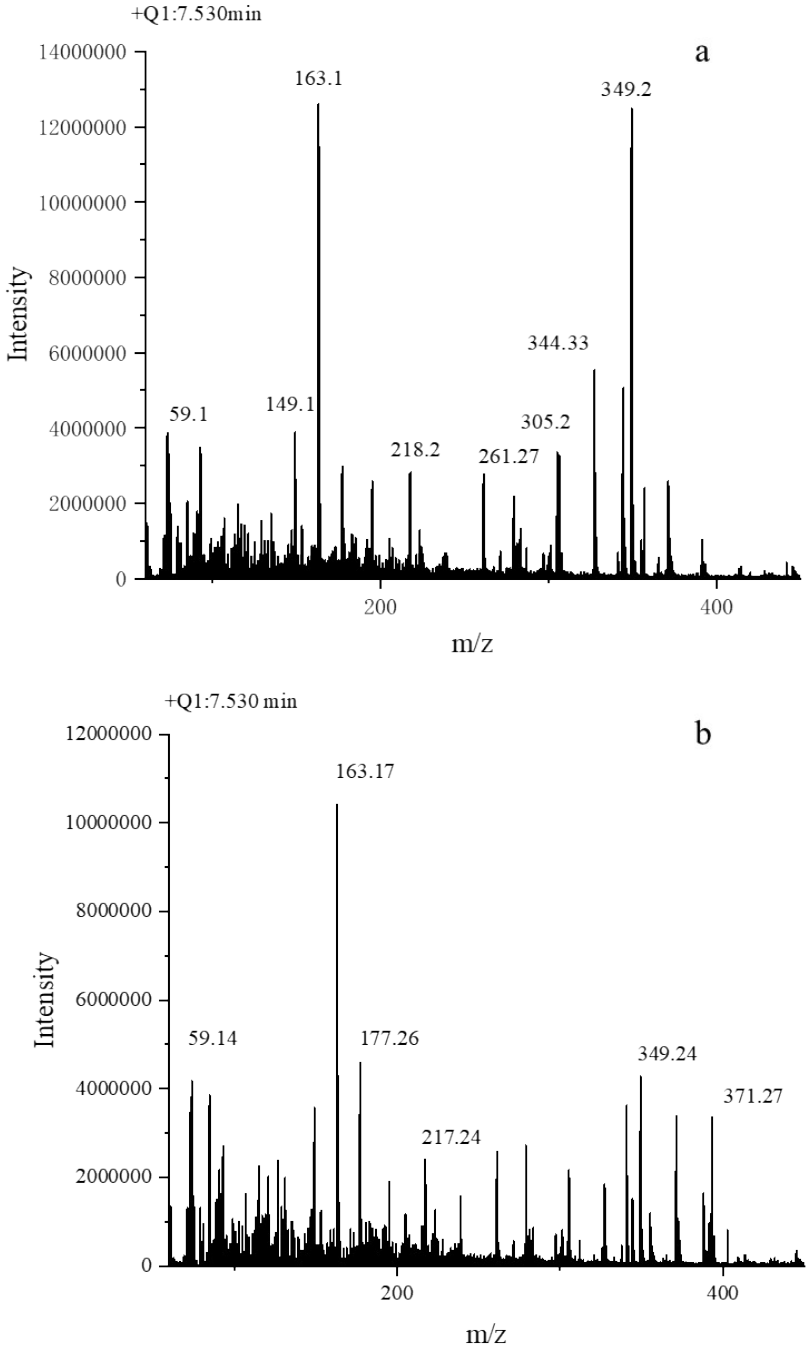


Fig S3 Mass spectra of SMX without HA (a) or with low-concentration HA (b) after 3 h-irradiation.

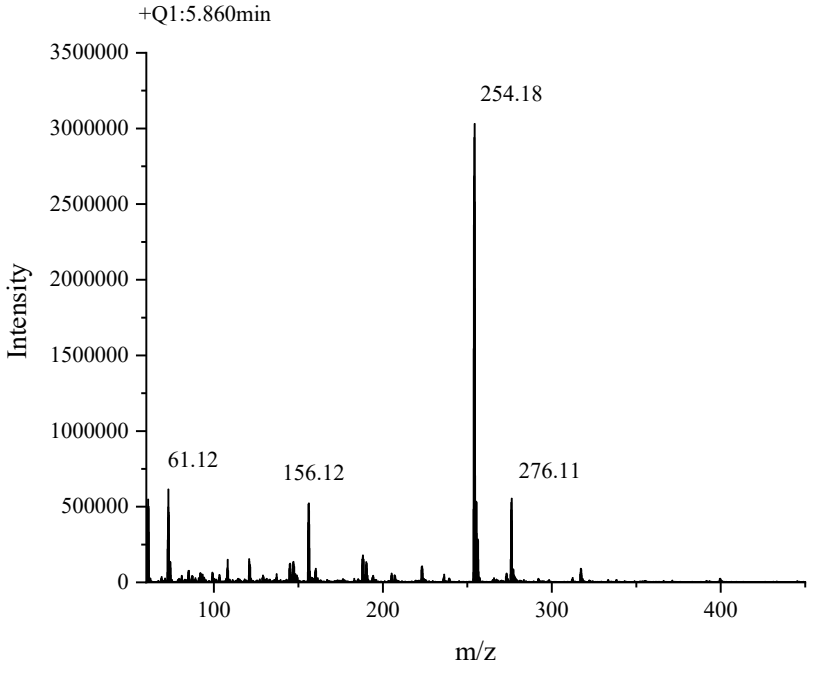


Fig S4 Mass spectra of SMX after 3 h-irradiation with high-concentration HA.

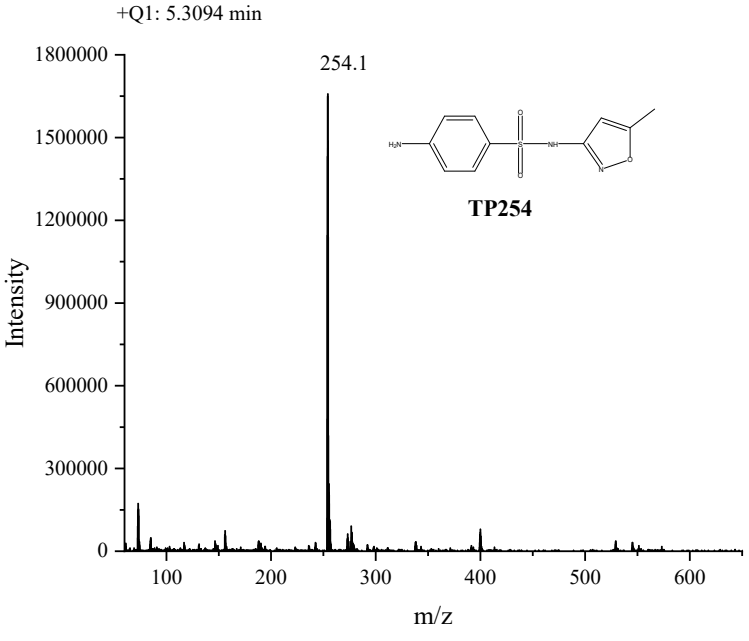


Fig. S5 Mass spectra of SMX degradation products TP 254.

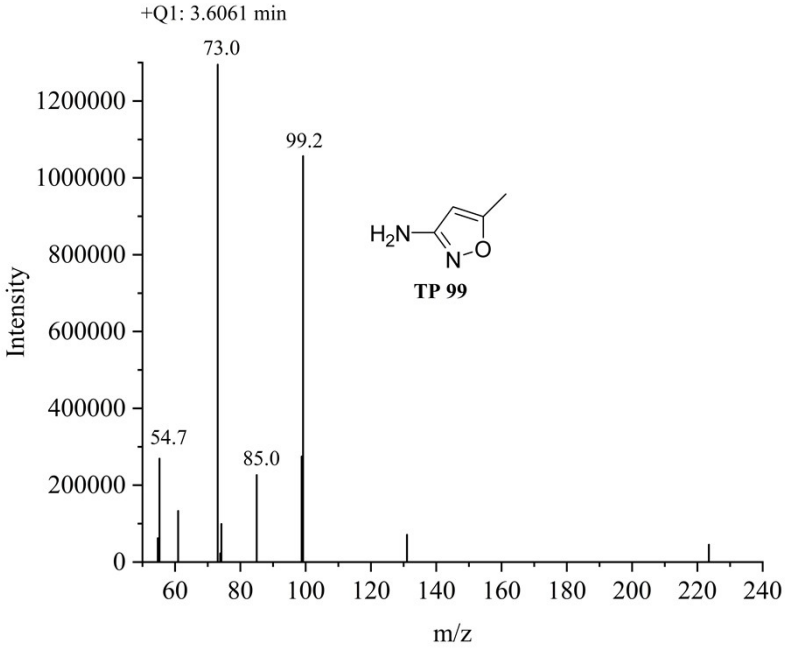


Fig. S6 Mass spectra of SMX degradation products TP 99.

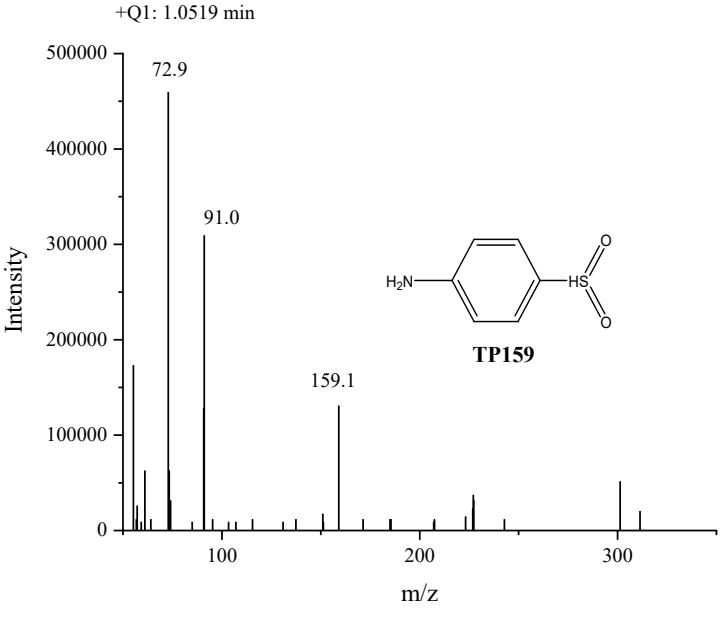


Fig. S7 Mass spectra of SMX degradation products TP159.

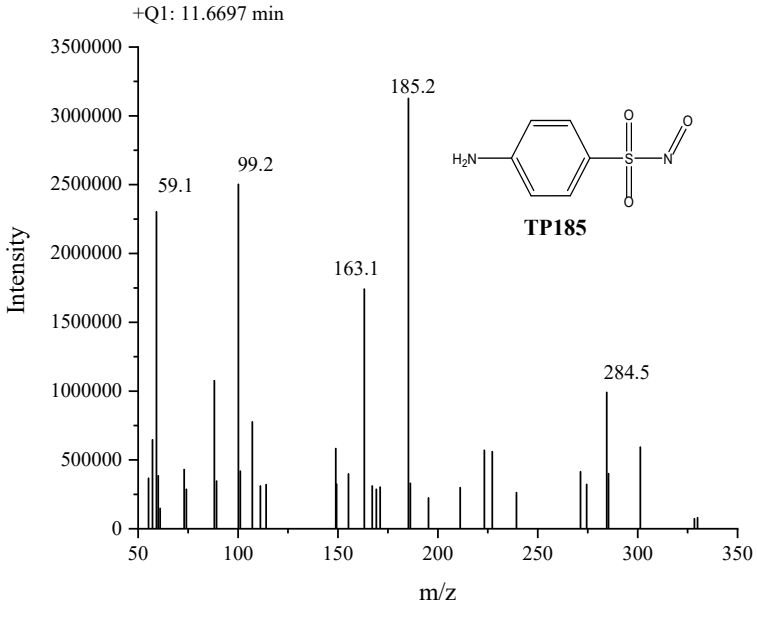


Fig. S8 Mass spectra of SMX degradation products TP185.

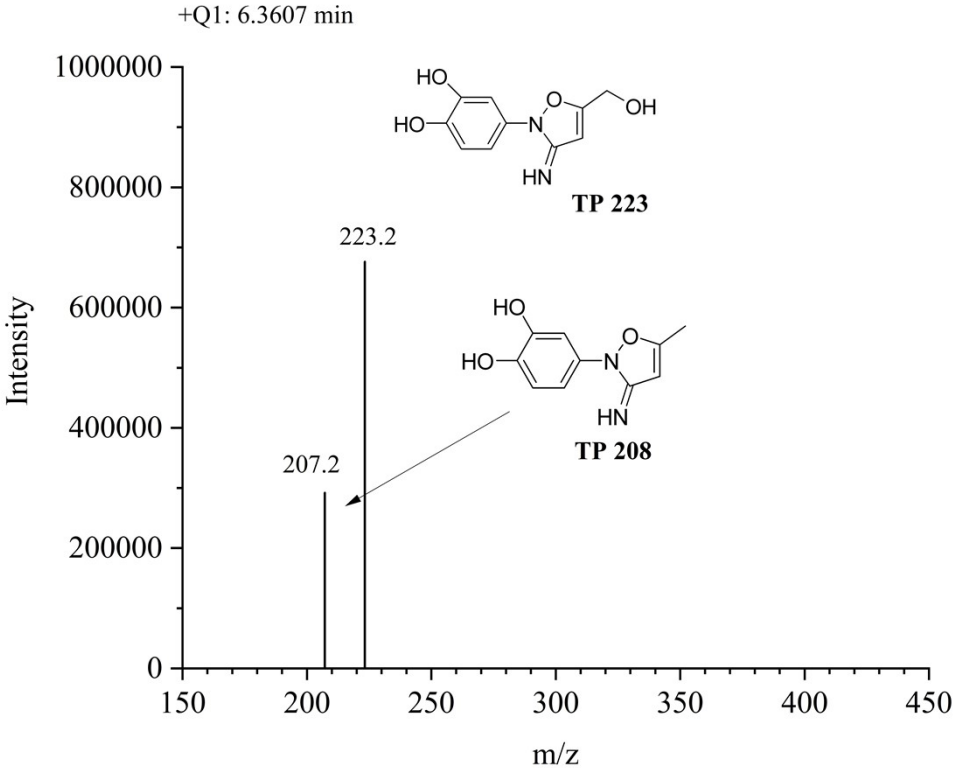


Fig. S9 Mass spectra of SMX degradation products TP 208 and TP 223.

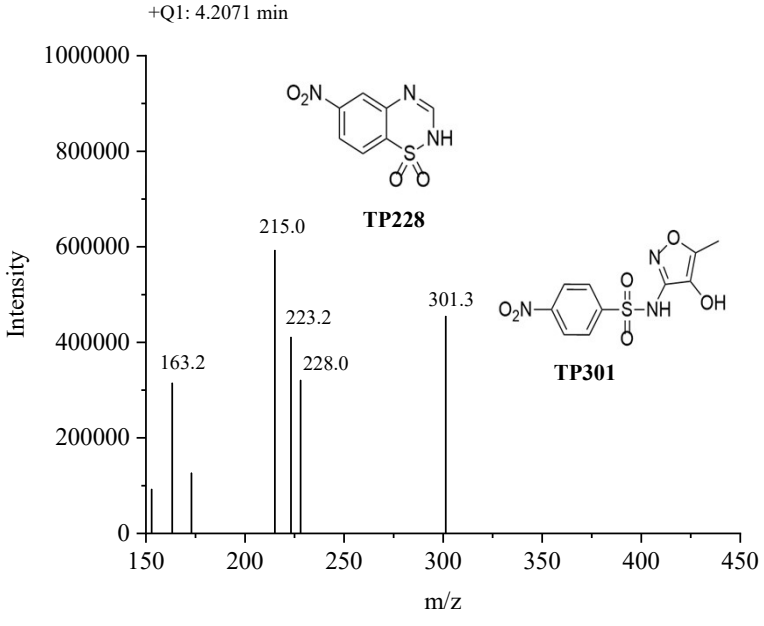


Fig. S10 Mass spectra of SMX degradation products TP 228 and TP 301.

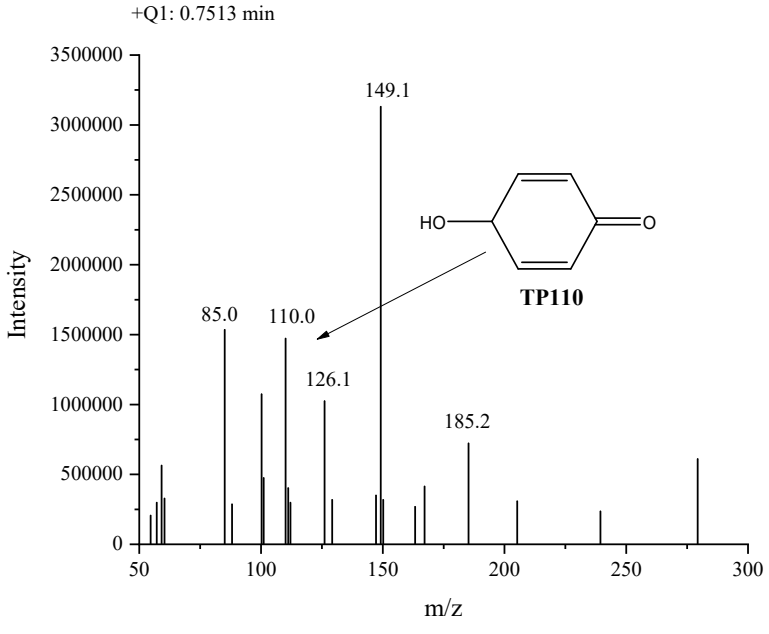


Fig. 11 Mass spectra of SMX degradation products TP110.

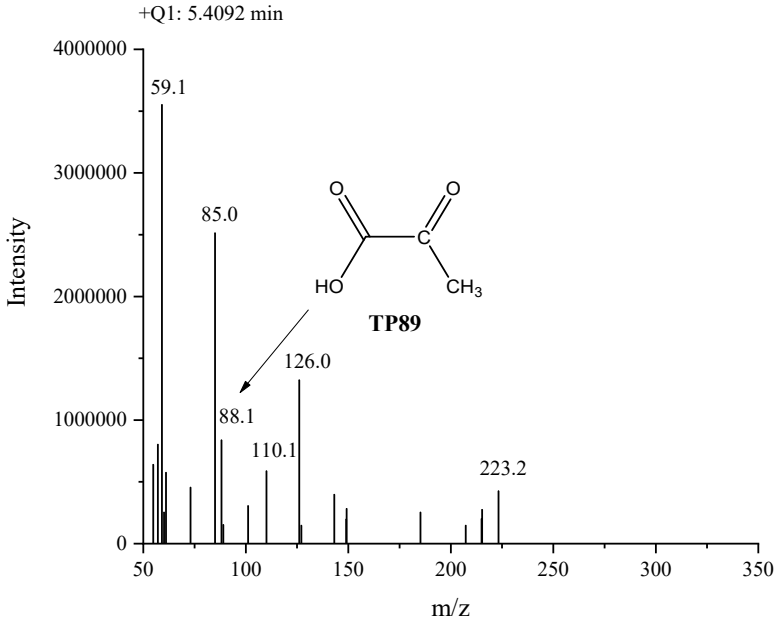


Fig. S12 Mass spectra of SMX degradation products TP89.

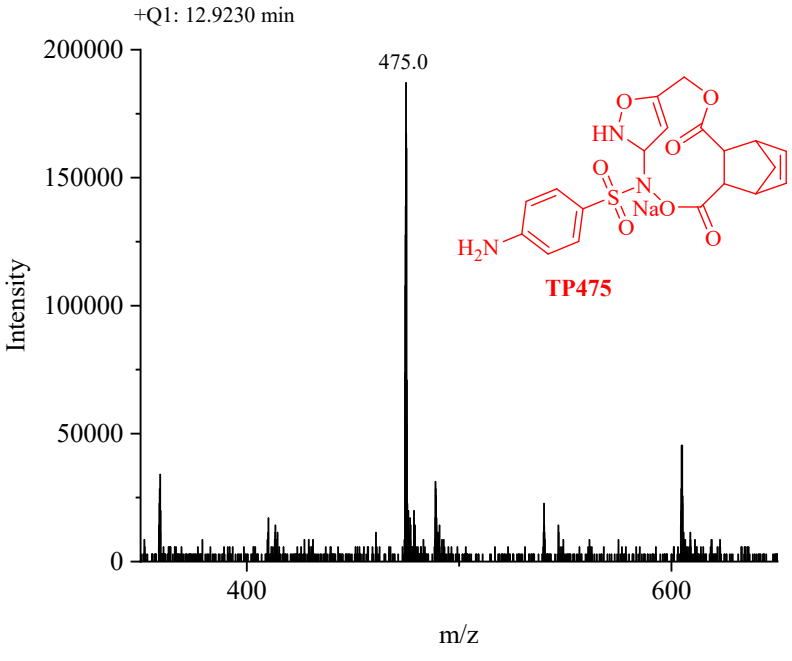


Fig. S13 Mass spectra of SMX degradation products TP 475.

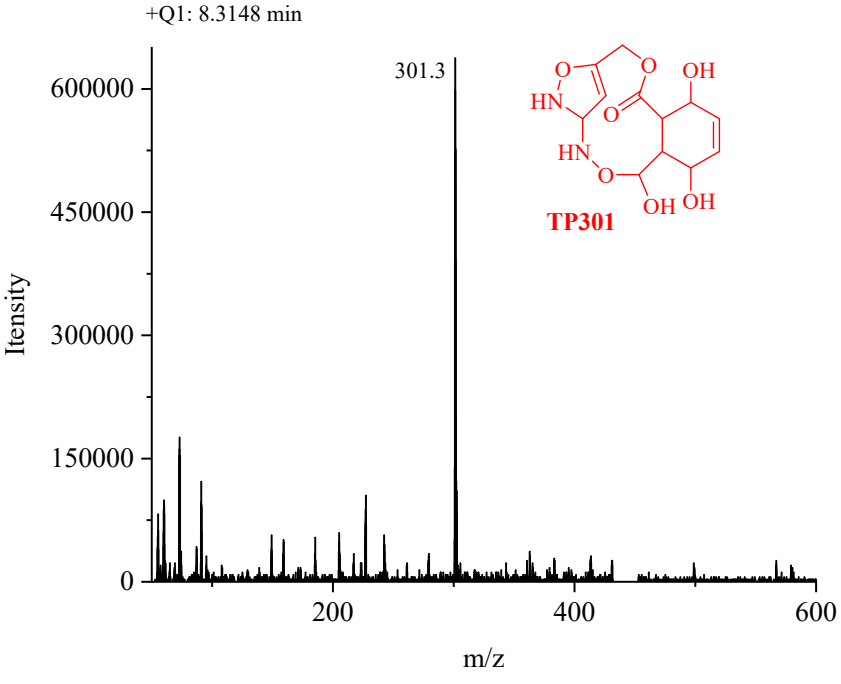


Fig. S14 Mass spectra of SMX degradation products TP 301.

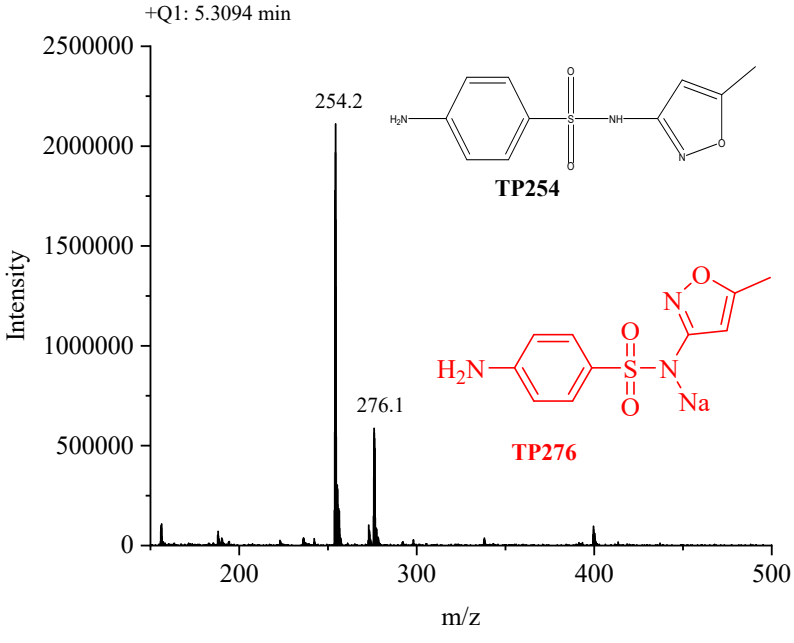


Fig. S15 Mass spectra of SMX degradation products TP 254 and TP 276.

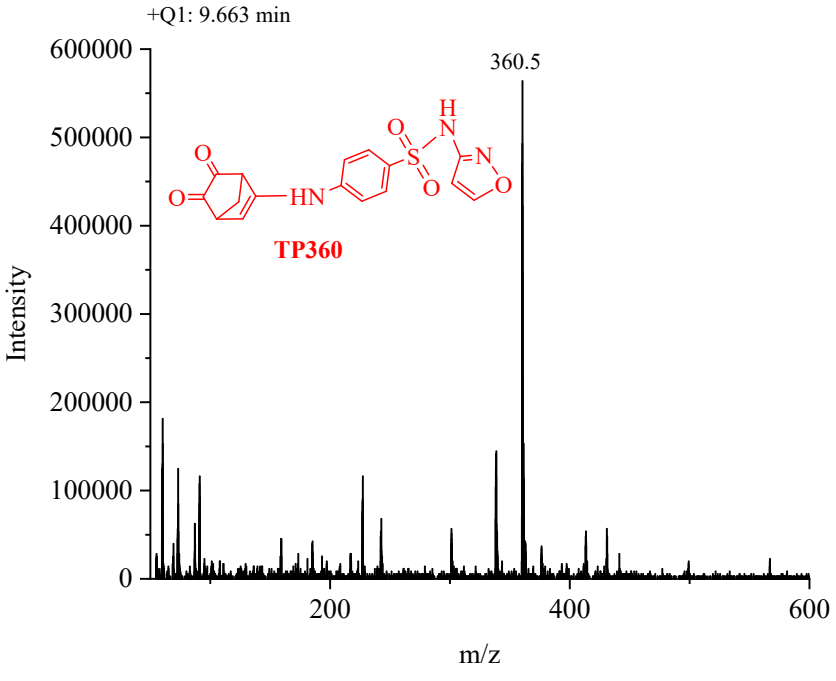


Fig. S16 Mass spectra of SMX degradation products TP360.

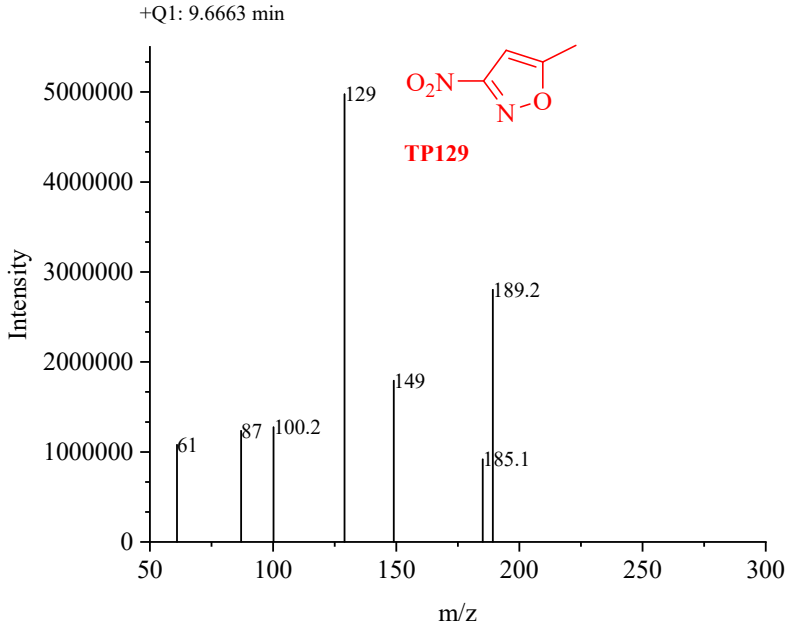


Fig. S17 Mass spectra of SMX degradation products TP 129.

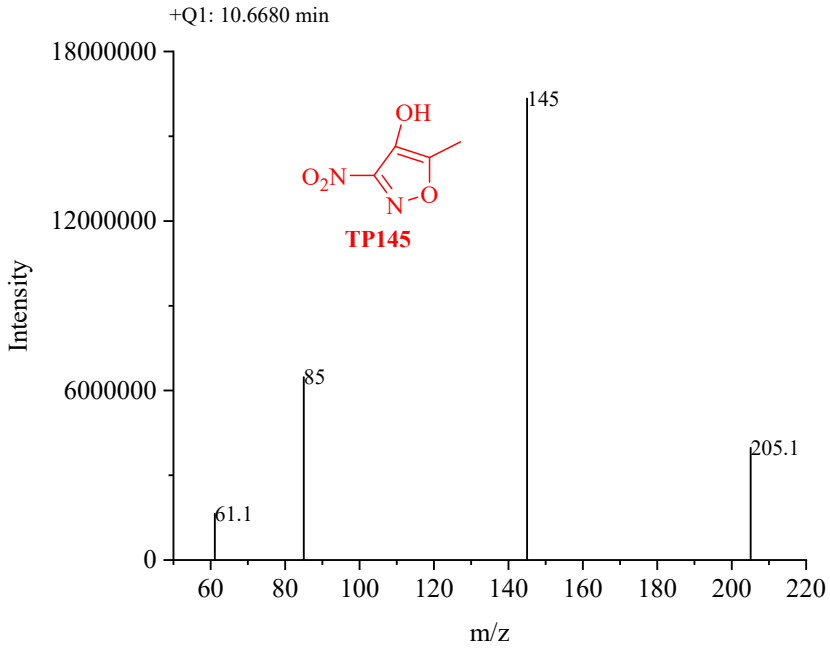


Fig. S18 Mass spectra of SMX degradation products TP 145.

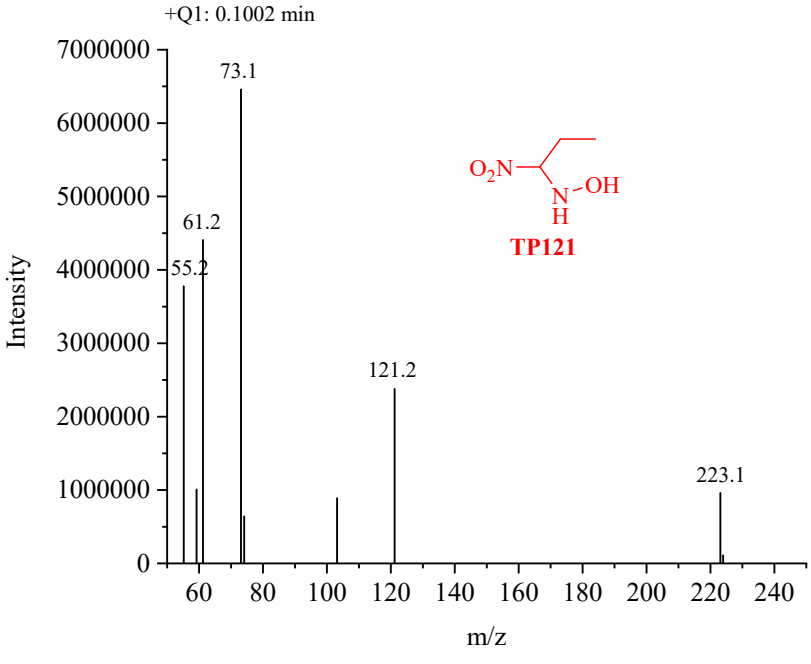


Fig. S19 Mass spectra of SMX degradation products TP 121.

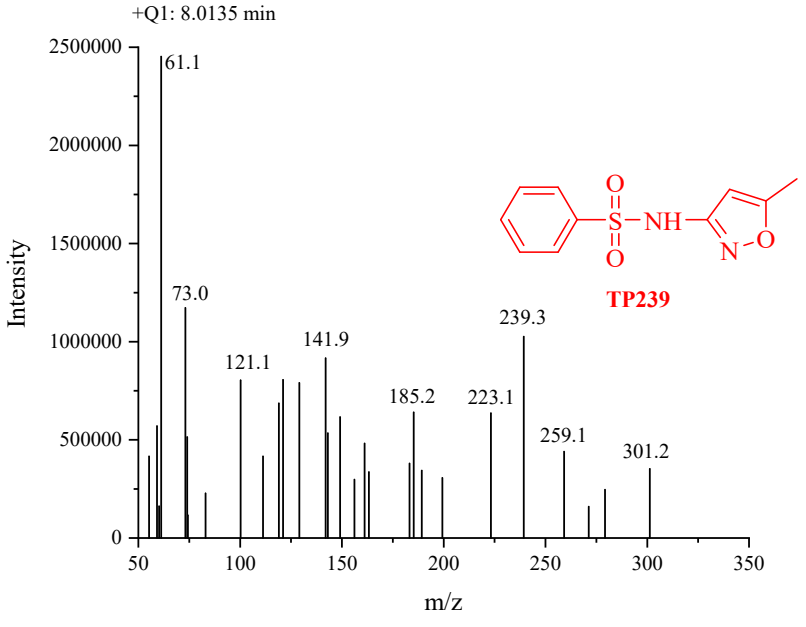


Fig. S20 Mass spectra of SMX degradation products TP 239.

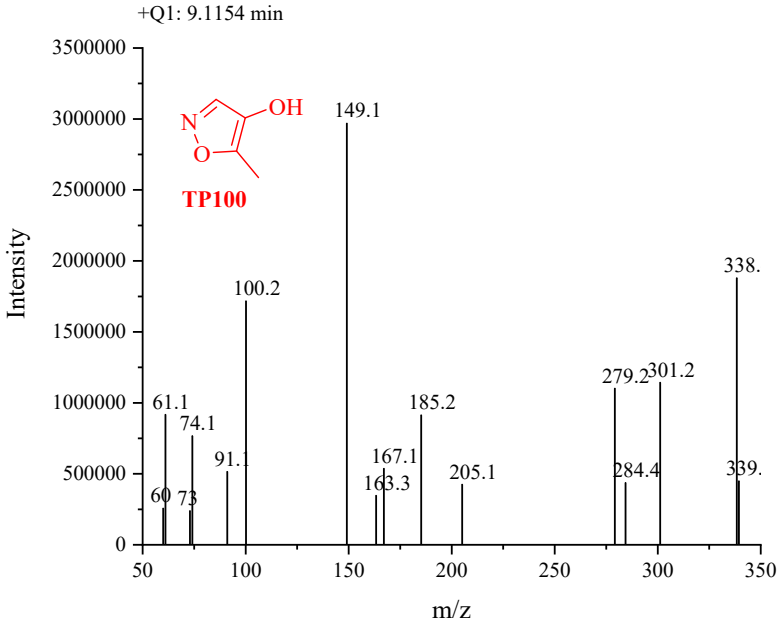


Fig. S21 Mass spectra of SMX degradation products TP 100.

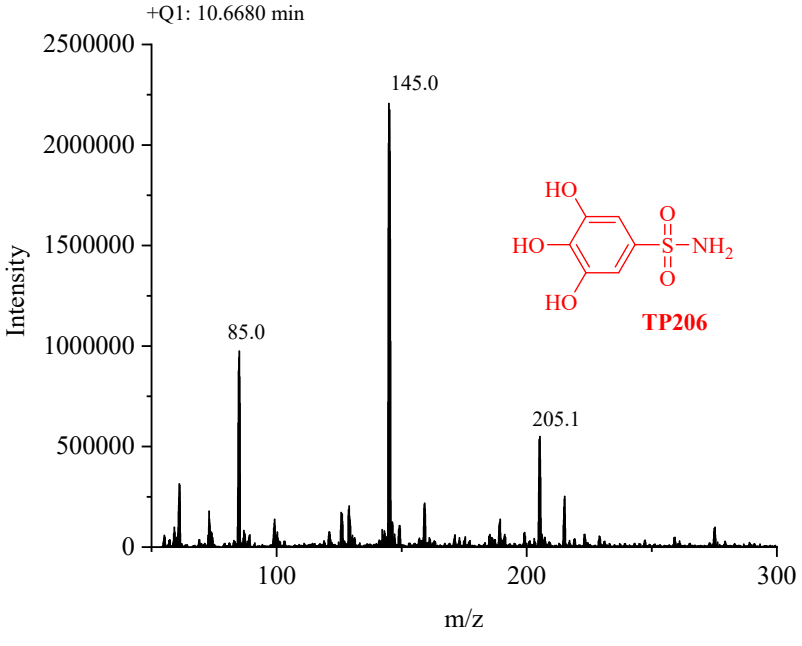


Fig. S22 Mass spectra of SMX degradation products TP 206.

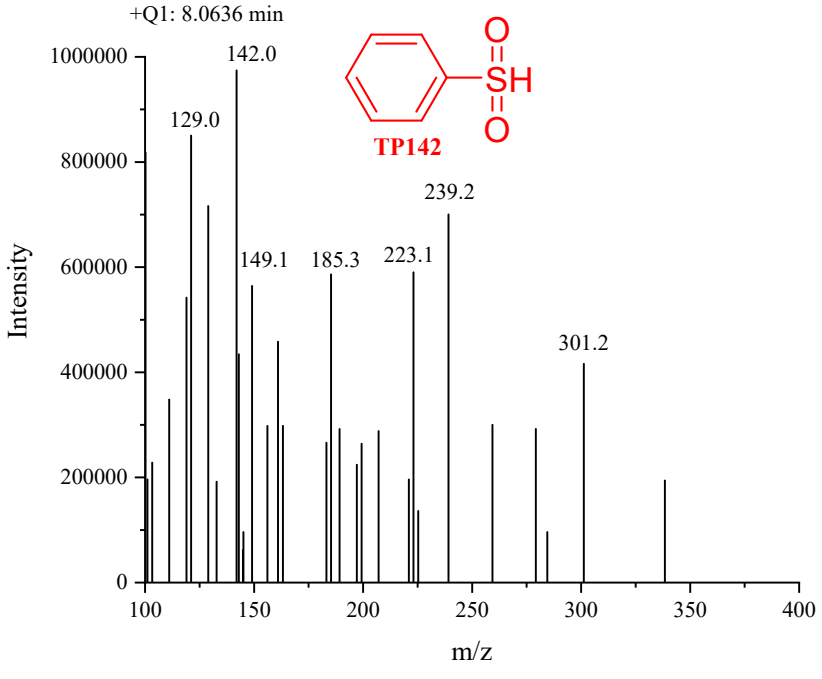


Fig. S23 Mass spectra of SMX degradation products TP 142.

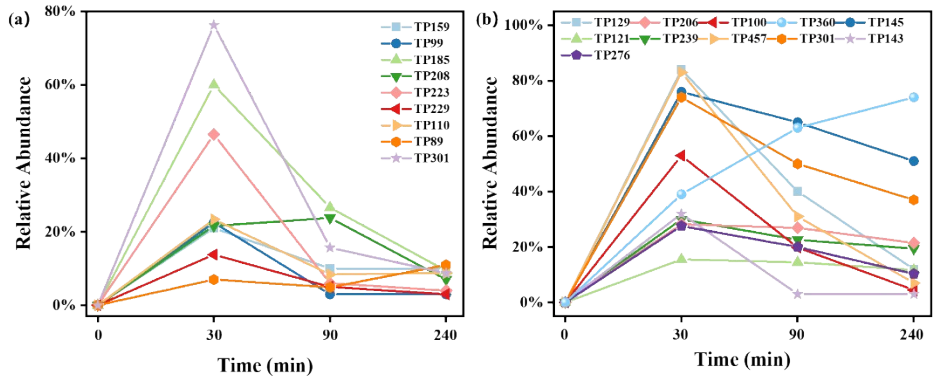


Fig. S24 The relative abundance of intermediates during SMX degradation: (a) without HA or with low-concentration HA; (b) with high-concentrations HA

Table S1 The kinetic parameters and half-life time of SMX photolysis.

Groups	k (min^{-1})	$t_{1/2}$ (min)	R^2
SMX	0.017 ± 0.0003^{d}	41.865 ± 0.8223	0.998
SMX+HA (1mg/L)	0.026 ± 0.0007^{a}	26.669 ± 0.7253	0.995
SMX+HA (10mg/L)	0.009 ± 0.0001^{h}	80.272 ± 0.3287	0.998
SMX+HA (50mg/L)	0.004 ± 0.0001^{ij}	196.67 ± 3.5506	0.999
SMX+HA (100mg/L)	0.001 ± 0.0001^{k}	489.005 ± 29.2207	0.847
SMX+IPA	0.011 ± 0.0001^{g}	61.314 ± 0.2685	0.984
SMX+THF	0.015 ± 0.0001^{de}	45.753 ± 0.2135	0.996
SMX + Sorbic acid	0.011 ± 0.0002^{g}	63.333 ± 0.2421	0.998
SMX+HA (1 mg/L) +IPA	0.013 ± 0.0001^{f}	52.593 ± 0.3863	0.999
SMX+HA (1 mg/L) +THF	0.025 ± 0.0006^{ab}	28.241 ± 0.6345	0.991
SMX+HA (1 mg/L) +Sorbic acid	0.019 ± 0.0004^{c}	37.363 ± 0.7262	0.999
SMX+HA (50 mg/L) +THF	0.004 ± 0.0003^{j}	163.229 ± 13.0051	0.982
SMX+HA (50 mg/L) +IPA	0.003 ± 0.0002^{i}	239.016 ± 0.5124	0.988
SMX+HA (50 mg/L) +Sorbic acid	0.003 ± 0.0002^{j}	223.878 ± 11.2346	0.990

Different letters in a row demonstrate significant difference among the groups at $p<0.05$

Table S2 Fukui function and CDD values of SMX without HA or with low-concentration HA.

SMX				
Atom	comdensed Fukui functions			
	f-	f+	f0	CDD
1(C）	0.0911	0.1161	0.1036	0.025
2(C）	0.0431	0.1067	0.0749	0.0636
3(C）	0.0902	0.0337	0.062	-0.0565
4(C）	0.0451	0.1096	0.0774	0.0645
5(C）	0.0912	0.1168	0.104	0.0256
6(C）	0.0725	0.0468	0.0597	-0.0256
7(H）	0.0363	0.0475	0.0419	0.0112
8(H）	0.0226	0.0416	0.0321	0.019
9(H）	0.0243	0.0439	0.0341	0.0196
10(H）	0.0363	0.0476	0.0419	0.0114
11(N）	0.1895	0.0277	0.1086	-0.1618
12(H）	0.0564	0.0166	0.0365	-0.0398
13(H）	0.0563	0.0165	0.0364	-0.0398
14(S）	0.0218	0.0169	0.0194	-0.0048
15(O）	0.0269	0.0227	0.0248	-0.0042
16(O）	0.0298	0.0215	0.0257	-0.0082
17(N）	0.0175	0.011	0.0143	-0.0065
18(H）	0.0109	0.0091	0.01	-0.0018
19(C）	0.006	0.0176	0.0118	0.0116
20(C）	0.005	0.0268	0.0159	0.0218
21(H）	0.0033	0.0088	0.006	0.0055
22(N）	0.0066	0.025	0.0158	0.0184
23(C）	0.0037	0.0205	0.0121	0.0167
24(O）	0.0078	0.0214	0.0146	0.0136
25(C）	0.0017	0.0079	0.0048	0.0062
26(H）	0.0014	0.0073	0.0044	0.0058
27(H）	0.0014	0.0077	0.0045	0.0064
28(H）	0.0013	0.0046	0.003	0.0033

Table S3 Fukui functions and CDD values of different SMX-HA complexes with high-concentration HA.

Atom	Configuration a				Configuration b				Configuration c			
	comdensed Fukui functions				comdensed Fukui functions				comdensed Fukui functions			
	f-	f+	f0	CDD	f-	f+	f0	CDD	f-	f+	f0	CDD
1(C)	0.0305	0.0085	0.0195	-0.022	0.0213	0.0078	0.0145	-0.0135	-0.0093	0.0087	-0.0003	0.018
2(C)	0.0142	0.0065	0.0104	-0.0077	0.0136	0.006	0.0098	-0.0075	-0.007	0.0149	0.004	0.0219
3(C)	0.0316	0.0064	0.019	-0.0252	0.0339	0.0052	0.0196	-0.0287	0.0089	0.0168	0.0129	0.008
4(C)	0.0164	0.0094	0.0129	-0.0069	0.0211	0.0131	0.0171	-0.008	0.0146	0.0202	0.0174	0.0055
5(C)	0.0306	0.0068	0.0187	-0.0239	0.0231	0.0085	0.0158	-0.0146	0.0136	0.0105	0.012	-0.0031
6(C)	0.0245	0.0144	0.0194	-0.0101	0.0123	0.0116	0.0119	-0.0007	0.0027	0.0143	0.0085	0.0116
11(N)	0.063	0.0118	0.0374	-0.0512	0.0472	0.0108	0.029	-0.0364	0.0103	-0.0001	0.0051	-0.0103
14(S)	0.0069	0.0075	0.0072	0.0005	0.0104	0.0169	0.0137	0.0065	0.0051	0.017	0.011	0.0119
15(O)	0.0197	0.0103	0.015	-0.0094	0.0256	0.022	0.0238	-0.0035	0.0205	0.0226	0.0215	0.0021
16(O)	0.0123	0.0087	0.0105	-0.0036	0.019	0.016	0.0175	-0.0031	-0.0021	0.0164	0.0072	0.0185
17(N)	0.0063	-0.0005	0.0029	-0.0068	0.006	0.0105	0.0083	0.0045	0.0047	0.0067	0.0057	0.002
19(C)	-0.0002	-0.0048	-0.0025	-0.0046	0.0087	0.0192	0.0139	0.0105	0.0084	0.0169	0.0126	0.0084
20(C)	0.0049	-0.0019	0.0015	-0.0068	0.0087	0.0298	0.0192	0.0211	0.0069	0.0287	0.0178	0.0218
22(N)	0.0024	0.0089	0.0057	0.0064	-0.0145	0.024	0.0047	0.0386	-0.0192	0.0146	-0.0023	0.0337
23(C)	-0.0031	0.0011	-0.001	0.0042	0.0015	0.0245	0.013	0.023	0.0028	0.0145	0.0086	0.0117
24(O)	0.0107	0.0068	0.0087	-0.0039	-0.0012	0.0184	0.0086	0.0195	-0.007	0.0191	0.006	0.0261
25(C)	0.0037	0.001	0.0023	-0.0027	0.0038	0.0092	0.0065	0.0054	0.0032	0.0096	0.0064	0.0063
29(C)	0.0746	0.0061	0.0403	-0.0685	0.0608	0.0057	0.0333	-0.0551	0.0894	0.0055	0.0475	-0.0839
30(C)	0.0108	0.0036	0.0072	-0.0072	0.0092	0.0022	0.0057	-0.0071	0.0192	0.0017	0.0105	-0.0175
31(C)	0.0119	0.0001	0.006	-0.0118	0.0177	0	0.0089	-0.0177	0.0166	0.0002	0.0084	-0.0164
32(C)	0.0112	0.0018	0.0065	-0.0094	0.0093	0.0014	0.0054	-0.0079	0.0117	-0.0007	0.0055	-0.0125
33(C)	0.0136	0.001	0.0073	-0.0126	0.0137	0.0014	0.0076	-0.0123	0.0162	0.0025	0.0093	-0.0137
34(C)	0.0747	-0.0043	0.0352	-0.079	0.067	-0.0009	0.0331	-0.0679	0.0806	0.0066	0.0436	-0.074
35(C)	0.0165	-0.0003	0.0081	-0.0168	0.0222	-0.0008	0.0107	-0.023	0.006	0.0037	0.0048	-0.0023
36(O)	0.0741	0.0045	0.0393	-0.0696	0.0418	0.0012	0.0215	-0.0406	0.0239	-0.0001	0.0119	-0.024
37(C)	0.0029	0.0066	0.0048	0.0036	0.0105	0.0052	0.0078	-0.0053	0.0338	0.0001	0.0169	-0.0337
38(O)	0.0222	-0.0013	0.0105	-0.0235	0.0532	0.0002	0.0267	-0.053	0.13	-0.0013	0.0643	-0.1313
39(O)	0.0399	0.0047	0.0223	-0.0352	0.084	0.0027	0.0434	-0.0813	0.0419	-0.0019	0.02	-0.0438
40(O)	0.0282	-0.0004	0.0139	-0.0286	0.0339	0.0031	0.0185	-0.0308	0.1246	0.0059	0.0653	-0.1187
41(C)	0.013	0.0057	0.0093	-0.0073	0.0124	0.0035	0.0079	-0.0089	0.0225	0.0019	0.0122	-0.0205
50(Na)	0.0338	0.7987	0.4162	0.7649	0.0481	0.6002	0.3241	0.5521	0.0377	0.0139	0.0258	0.0238
51(Na)	0.026	0.0115	0.0188	-0.0144	0.025	0.009	0.017	-0.016	0.035	0.5754	0.3052	0.5404

Table S4 Degradation intermediates of SMX without HA and with low-concentration HA

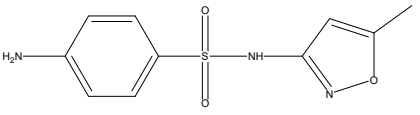
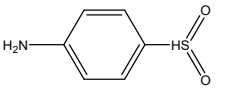
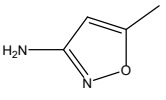
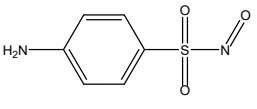
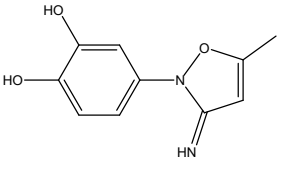
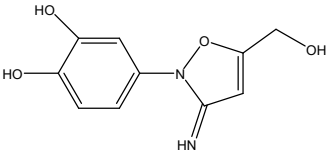
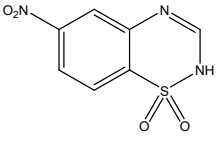
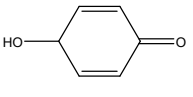
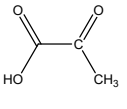
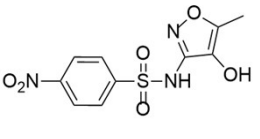
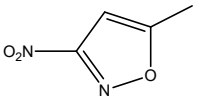
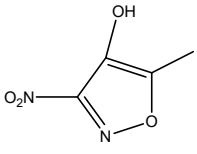
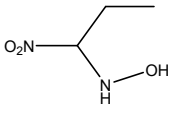
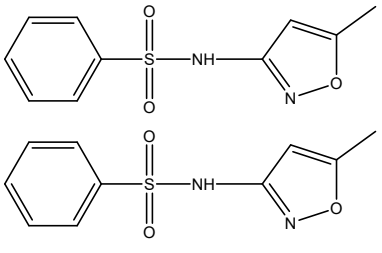
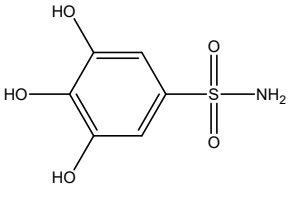
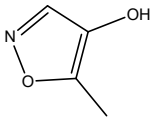
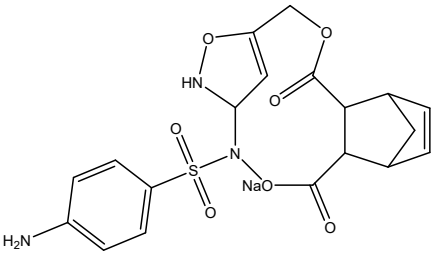
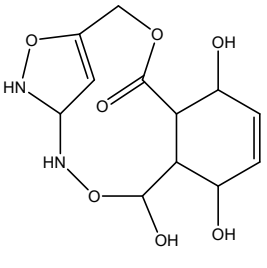
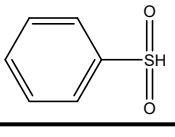
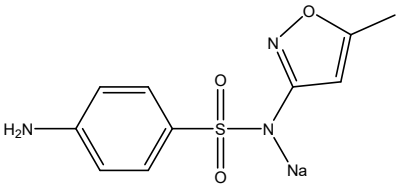
Compound	$[M+H]^+$	Retention time (min)	Proposed formula	Molecular structure
TP254	254	5.3	$C_{10}H_{11}N_3O_3S$	
TP159	159	1.0	$C_6H_7NO_2S$	
TP99	99	3.6	$C_4H_6N_2O$	
TP185	185	11.6	$C_6H_6N_2O_3S$	
TP208	207	6.3	$C_{10}H_{10}N_2O_3$	
TP223	223	6.3	$C_{10}H_{10}N_2O_4$	
TP229	228	4.2	$C_7H_5N_3O_4S$	
TP110	110	0.7	$C_6H_6O_2$	
TP89	88	5.4	$C_3H_4O_3$	
TP301	301	0.7	$C_{10}H_9N_3O_6S$	

Table S5 Degradation intermediates of SMX with high-concentrations HA

Compound	$[M+H]^+$	Retention time (min)	Proposed formula	Molecular structure
TP129	129	9.6	$C_4H_4N_2O_3$	
TP145	145	10.6	$C_4H_4N_2O_4$	
TP121	121	0.1	$C_3H_8N_2O_3$	
TP239	239	8.0	$C_{10}H_{10}N_2O_3S$	
TP206	205	10.6	$C_6H_7NO_5S$	
TP100	100	9.1	$C_4H_5NO_2$	
TP457	457	12.9	$C_{19}H_{19}N_3NaO_7S$	
TP301	301	8.3	$C_{12}H_{16}N_2O_7$	
TP143	142	8.0	$C_6H_6O_2S$	

TP276	276	5.3	$C_{10}H_{10}N_3NaO_3S$	
TP360	360	9.6	$C_{16}H_{13}N_3O_5S$