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Investigation of occurrence, elimination and degradation of pharmaceutical and personal care products in drinking water using liquid chromatography-tandem mass spectrometry

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Table 1.1 Selected pharmaceutical compounds and their general information.

Compounds	Formula	CAS #	Molecular weight	Class
acetaminophen	$C_8H_9NO_2$	103-90-2	151.2	analgesics
caffeine	$C_8H_{10}N_4O_2$	58-08-2	194.2	stimulant
carbamazepine	$C_{15}H_{12}N_2O$	298-46-4	236.3	anticonvulsant
clofibrilic acid	$C_{10}H_{11}ClO_3$	882-09-07	214.7	lipid-regulator
codeine	$C_{18}H_{21}NO_3$	76-57-3	299.4	analgesics
estradiol	$C_{18}H_{24}O_2$	50-28-2	272.4	hormone
estriol	$C_{18}H_{24}O_3$	50-27-1	288.4	hormone
estrone	$C_{18}H_{22}O_2$	53-16-7	270.4	hormone
ethynylestradiol	$C_{20}H_{24}O_2$	57-63-6	296.4	hormone
ibuprofen	$C_{13}H_{18}O_2$	15687-27-1	206.3	analgesics
iopromide	$C_{18}H_{24}I_3N_3O_8$	107793-72-6	791.1	X-ray contrast media
lincomycin	$C_{18}H_{34}N_2O_6S$	154-21-2	406.5	antibiotics
sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	723-46-6	253.3	antibiotics
triclosan	$C_{12}H_7Cl_3O_2$	3380-34-5	289.5	antibiotics
trimethoprim	$C_{14}H_{18}N_4O_3$	738-70-5	290.3	antibiotics
tylosin	$C_{46}H_{77}NO_{17}$	1401-69-0	916.1	antibiotics

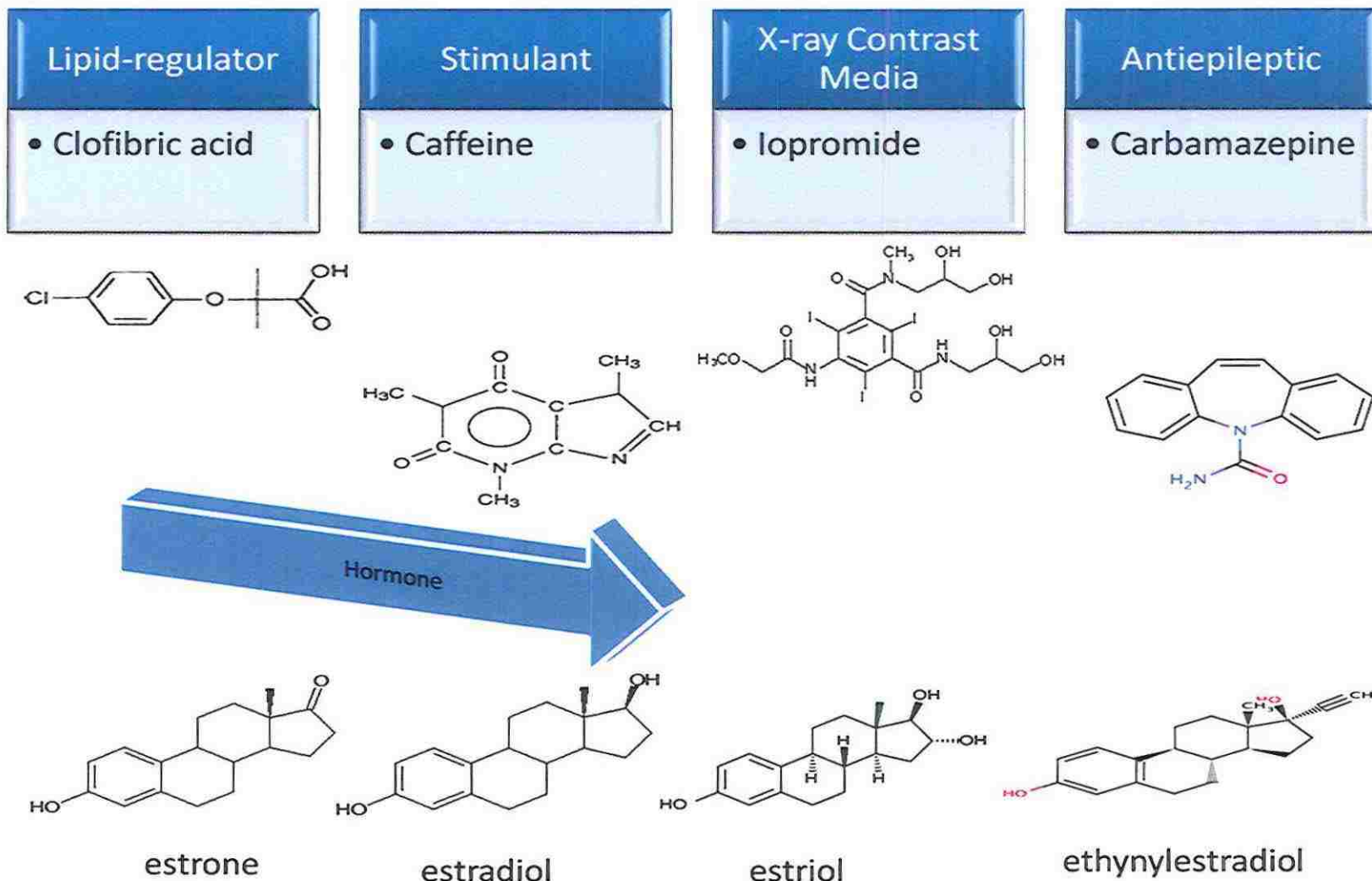


Figure 1.1 Compound structures of sixteen pharmaceuticals.

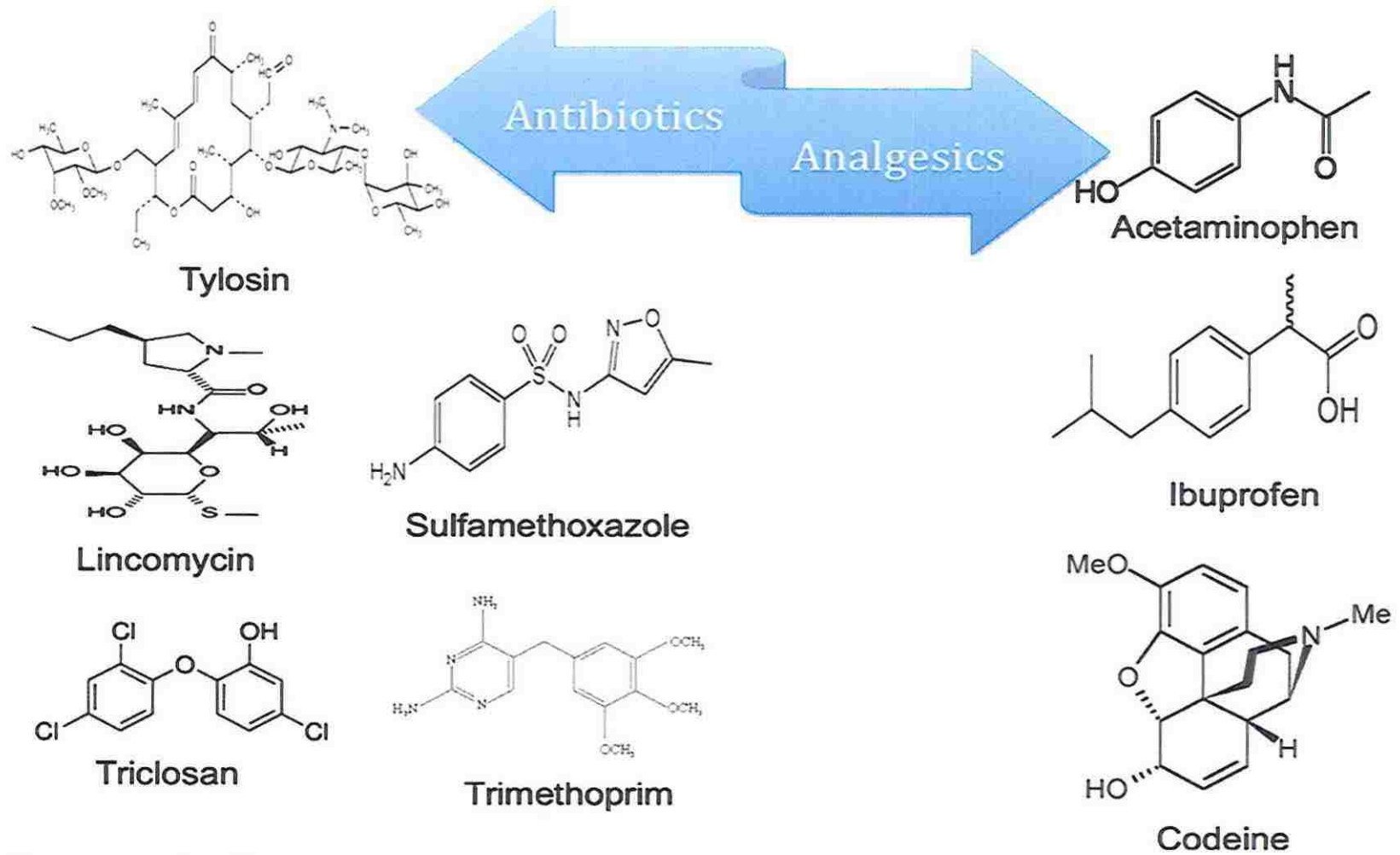


Figure 1.1 (continued).

PAPER

1. Investigation of Pharmaceuticals in Missouri Natural and Drinking Water Using High Performance Liquid Chromatography-Tandem Mass Spectrometry

ABSTRACT

A comprehensive method has been developed and validated in two different water matrices for the analysis of 16 pharmaceutical compounds using solid phase extraction (SPE) of water samples, followed by liquid chromatography coupled with tandem mass spectrometry. These 16 compounds include antibiotics, hormones, analgesics, stimulants, antiepileptics, and X-ray contrast media. Method detection limits (MDLs) that were determined in both reagent water and municipal tap water ranged from 0.1 to 9.9 ng/L. Recoveries for most of the compounds were comparable to those obtained using U.S. EPA methods. Treated and untreated water samples were collected from 31 different water treatment facilities across Missouri, in both winter and summer seasons, and analyzed to assess the 16 pharmaceutical compounds. The results showed that the highest pharmaceutical concentrations in untreated water were caffeine, ibuprofen, and acetaminophen, at concentrations of 224, 77.2, and 70 ng/L, respectively. Concentrations of pharmaceuticals were generally higher during the winter months, as compared to those in the summer due, presumably, to smaller water quantities in the winter, even though pharmaceutical loadings into the receiving waters were similar for both seasons.

Table 1. Sixteen pharmaceutical compounds and their general information.

Compounds	Formula	CAS #	Molecular weight
acetaminophen	$C_8H_9NO_2$	103-90-2	151.2
caffèine	$C_8H_{10}N_4O_2$	58-08-2	194.2
carbamazepine	$C_{15}H_{12}N_2O$	298-46-4	236.3
clofibrac acid	$C_{10}H_{11}ClO_3$	882-09-07	214.7
codeine	$C_{18}H_{21}NO_3$	76-57-3	299.4
estradiol	$C_{18}H_{24}O_2$	50-28-2	272.4
estriol	$C_{18}H_{24}O_3$	50-27-1	288.4
estrone	$C_{18}H_{22}O_2$	53-16-7	270.4
ethynylestradiol	$C_{20}H_{24}O_2$	57-63-6	296.4
ibuprofen	$C_{13}H_{18}O_2$	15687-27-1	206.3
iopromide	$C_{18}H_{24}I_3N_3O_8$	107793-72-6	791.1
lincomycin	$C_{18}H_{34}N_2O_6S$	154-21-2	406.5
sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	723-46-6	253.3
triclosan	$C_{12}H_7Cl_3O_2$	3380-34-5	289.5
trimethoprim	$C_{14}H_{18}N_4O_3$	738-70-5	290.3
tylosin	$C_{46}H_{77}NO_{17}$	1401-69-0	916.1

Table 2. LC-MS/MS experimental conditions of the sixteen pharmaceutical compounds.

Compounds	Retention time (min)	ESI mode	Precursor ion	Product ion	Decustering potential (V)	Collision energy (V)	Collision cell exit potential (V)	Internal standard
acetaminophen	5.7	positive	151.8	110	66	25	6	¹³ C ₃ -caffèine
caffèine	8.2	positive	194.9	138	51	31	8	¹³ C ₃ -caffèine
carbamazepine	11.7	positive	236.9	194	71	31	12	¹³ C ₃ -trimethoprim
clofibrac acid	8.1	negative	212.9	126.8	-40	-24	-7	¹³ C ₃ -ibuprofen
codeine	7.9	positive	300	215	81	37	14	¹³ C ₃ -trimethoprim
estradiol	13.1	positive	255	159	76	29	10	¹³ C ₃ -caffèine
estriol	8.8	negative	286.7	171.1	-100	-50	-9	¹³ C ₆ -estrone
estrone	12	negative	268.9	144.8	-110	-54	-7	¹³ C ₆ -estrone
ethynylestradiol	13.8	positive	279	133.2	61	27	8	¹³ C ₃ -caffèine
ibuprofen	9.5	negative	204.9	159	-55	-10	-10	¹³ C ₃ -ibuprofen
iopromide	3.5	negative	789.9	126.7	-85	-48	-5	¹³ C ₃ -ibuprofen
lincomycin	8	positive	407.1	126.2	76	39	6	¹³ C ₃ -trimethoprim
sulfamethoxazole	10.2	positive	253.9	156	61	25	10	¹³ C ₃ -trimethoprim
triclosan	15.8	negative	286.7	35	-50	-110	-3	¹³ C ₆ -estrone
trimethoprim	8.3	positive	291	230.2	81	35	14	¹³ C ₃ -trimethoprim
tylosin	10.6	positive	916.5	174.1	136	55	10	¹³ C ₃ -caffèine

Table 3. Method detection limits (MDL), spike recovery and relative standard deviation (RSD) of studied pharmaceuticals in reagent water (Deionized (DI)) water and tap water matrix (n=9).

Compound	MDL (ng/L)		High-level spike						Low-level spike					
	DI Water	Tap Water	DI water			Tap Water			DI water			Tap Water		
			Spike (ng/L)	Recovery (%)	RSD (%)	Spike (ng/L)	Recovery (%)	RSD (%)	Spike (ng/L)	Recovery (%)	RSD (%)	Spike (ng/L)	Recovery (%)	RSD (%)
acetaminophen	2.7	1.4	200	95.8	10.4	200	100	6.9	10	106	8.8	10	73.9	6.4
caffeine	0.8	1.1	400	109	9.1	400	115	8.5	2	46.4	29	2	50.7	37.4
carbamazepine	0.5	0.2	200	104	4.9	200	121	5.3	1	125	13	1	125	5.9
clofibric acid	1.3	0.6	400	122	12.9	400	157	7.4	1	72.6	28.1	1	56.7	37.5
codeine	1.0	1.5	400	104	2.6	400	122	4.5	5	145	4.7	5	150	6.7
estradiol	0.8	1.2	400	95.6	5	400	106	4.4	5	102	5.3	5	97.9	8.7
estriol	4.3	5.2	200	128	4.9	200	115	2.4	20	120	6.2	20	121	7.4
estrone	1.4	1.0	200	116	2.6	200	109	1.9	2	89.2	26	2	123	13.9
ethynylestradiol	0.1	0.5	200	92.3	6.2	200	102	2.8	1	108	4.4	1	75.8	22
ibuprofen	1.0	1.6	400	119	1.9	400	110	2.2	20	106	3.5	20	85.9	3.3
iopromide	3.5	9.9	200	98.1	8.8	200	90.6	7.8	20	136	4.4	20	153	11.2
lincomycin	0.1	0.1	200	103	9.9	200	97.5	5.6	1	12.6	32.8	1	7.1	55.2
sulfamethoxazole	0.4	0.3	400	90	11.5	400	102	4.7	1	90.5	14.8	1	92.7	9.3
triclosan	1.0	1.2	400	32	14.1	400	33.6	15.7	10	39.3	8.7	10	29.8	13.2
trimethoprim	0.3	0.4	400	123	11.3	400	125	4.9	1	91.2	12.2	1	91.2	14
tylosin	0.3	0.2	200	44.6	14.8	200	48.6	30.8	1	18.2	51.2	1	15.1	37.8

Table 4. Pharmaceutical concentration of real water samples in winter season.

ID #	Water source	Treatment	Sample type	Concentration (ng/L)										
				Tylo-sin	Linco-mycin	Trimetho-prim	Sulfameth-oxazole	Acetamin-ophen	Caf-feine	Carbama-zepine	Code-ine	Triclo-san	Ibup-rofen	Iopr-omide
1	MS River	Free chlorine	Untreated	<MDL	4.2	4.6	13.7	5.3	47.2	8.4	<MDL	<MDL	16.6	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	13.0	2.2	<MDL	<MDL	8.8	<MDL
2	MS River	Chloramines	Untreated	<MDL	<MDL	7.7	28.8	21.8	106.0	8.7	<MDL	<MDL	37.5	22.4
			Treated	<MDL	<MDL	<MDL	1.5	<MDL	54.4	3.9	<MDL	<MDL	26.6	<MDL
3	MO River	Chloramines	Untreated	<MDL	1.8	2.8	18.8	16.0	49.6	5.5	<MDL	2.1	27.1	<MDL
			Treated	<MDL	<MDL	1.7	8.2	<MDL	36.0	4.7	<MDL	<MDL	23.4	<MDL
4	Alluvial GW	Chloramines	Untreated	<MDL	1.1	<MDL	5.5	<MDL	14.8	3.2	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	2.5	<MDL	<MDL	<MDL	<MDL	<MDL
5	Alluvial GW	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	50.0	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	43.6	<MDL	<MDL	<MDL	<MDL	<MDL
6	Deep rock wells	Chloramines	Untreated	<MDL	<MDL	<MDL	2.8	<MDL	11.4	1.9	<MDL	9.8	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	3.4	<MDL	<MDL	2.8	<MDL	<MDL
7	Deep rock wells	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	18.2	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	4.5	<MDL	<MDL	<MDL	<MDL	<MDL
8	Reservoirs	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	10.3	<MDL	<MDL	3.4	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	8.8	<MDL	<MDL	<MDL	<MDL	<MDL
9	Reservoir	Chloramines	Untreated	<MDL	2.5	<MDL	<MDL	14.2	157.2	1.0	<MDL	<MDL	2.4	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	18.4	<MDL	<MDL	<MDL	2.0	<MDL
10	MO River	Chloramines	Untreated	<MDL	2.9	9.1	38.1	56.0	224.8	8.1	3.7	<MDL	77.2	<MDL
			Treated	<MDL	<MDL	<MDL	4.8	<MDL	180.8	6.8	<MDL	<MDL	72.8	<MDL

ND = No Data

MDL = Method Detection Limit

Table 4. (continued)

ID #	Water source	Treatment	Sample type	Concentration (ng/L)										
				Tylo-sin	Linco-mycin	Trimetho-prim	Sulfameth-oxazole	Acetamin-ophen	Caf-feine	Carbama-zepine	Code-ine	Triclo-san	Ibup-rofen	Iopr-omide
11	MS River	Free chlorine	Untreated	<MDL	2.8	4.0	18.2	11.6	39.0	8.1	3.0	<MDL	13.6	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	28.0	32.9	3.2	<MDL	<MDL	10.4	<MDL
12	Lake	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	20.1	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	8.9	<MDL	<MDL	<MDL	<MDL	<MDL
13	Lake	Chloramines	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	21.3	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	4.0	<MDL	<MDL	<MDL	<MDL	<MDL
14	Lake	Chloramines	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	29.4	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	4.3	<MDL	<MDL	<MDL	<MDL	<MDL
15	Deep Well	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	6.2	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	6.5	<MDL	<MDL	<MDL	<MDL	<MDL
16	Deep Well	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	3.0	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	4.4	<MDL	<MDL	<MDL	<MDL	<MDL
17	Deep Well	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	2.9	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	2.6	<MDL	<MDL	<MDL	<MDL	<MDL
18	Deep Well	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	2.7	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	3.0	<MDL	<MDL	<MDL	<MDL	<MDL
19	Lake	Free chlorine	Untreated	<MDL	<MDL	<MDL	1.7	<MDL	11.1	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
20	Unconsolidated Wells	Free chlorine	Untreated	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	2.8	<MDL	<MDL	<MDL	<MDL	<MDL

ND = No Data

MDL = Method Detection Limit

Table 4. (continued)

ID #	Water source	Treatment	Sample type	Concentration (ng/L)										
				Tylo-sin	Linco-mycin	Trimetho-prim	Sulfameth-oxazole	Acetamin-ophen	Caf-feine	Carbama-zepine	Code-ine	Triclo-san	Ibup-rofen	Iopr-omide
21	Unconsolidated Wells	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	5.6	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	7.2	<MDL	<MDL	<MDL	<MDL	<MDL
22	Unconsolidated Wells	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	34.4	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	9.3	<MDL	<MDL	<MDL	<MDL	<MDL
23	Unconsolidated Wells	Free chlorine	Untreated	<MDL	1.1	<MDL	7.2	<MDL	39.1	3.3	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	3.2	<MDL	<MDL	<MDL	<MDL	<MDL
24	Lake	Free chlorine	Untreated	4.3	<MDL	<MDL	<MDL	<MDL	6.7	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	4.8	<MDL	<MDL	<MDL	<MDL	<MDL
25	Lake	Chloramines	Untreated	<MDL	7.7	<MDL	<MDL	<MDL	27.7	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	3.7	<MDL	<MDL	<MDL	<MDL	<MDL
26	Lake	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	7.9	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	7.4	<MDL	<MDL	<MDL	<MDL	<MDL
27	Reservoir	Free chlorine	Untreated	<MDL	<MDL	<MDL	3.1	70.0	10.0	4.8	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	6.0	3.5	<MDL	<MDL	<MDL	<MDL
28	Lake	Free chlorine	Untreated	<MDL	1.1	<MDL	<MDL	<MDL	11.3	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	6.5	<MDL	<MDL	<MDL	<MDL	<MDL
29	River	Chloramines	Untreated	<MDL	<MDL	<MDL	6.1	19.4	31.5	3.2	<MDL	<MDL	4.4	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	20.4	1.4	<MDL	<MDL	3.2	<MDL
30	Lake	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	16.9	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	3.8	<MDL	<MDL	<MDL	<MDL	<MDL
31	Lake	Chloramines	Untreated	<MDL	<MDL	2.1	<MDL	<MDL	10.8	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	5.2	<MDL	<MDL	<MDL	<MDL	<MDL

ND = No Data

MDL = Method Detection Limit

Table 5. Pharmaceutical concentration of real water samples in summer season.

ID #	Water source	Treatment	Sample type	Concentration (ng/l)										
				Tylo-sin	Linco-mycin	Trimetho-prim	Sulfameth-oxazole	Acetamin-ophen	Caf-feine	Carbama-zepine	Cod-eine	Triclo-san	Ibupro-fen	Iprom-ide
1	MS River	Free chlorine	Untreated	<MDL	2.6	<MDL	4.2	<MDL	15.6	5.7	<MDL	3.1	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	9.5	1.0	<MDL	<MDL	<MDL	<MDL
2	MS River	Chloramines	Untreated	<MDL	4.6	<MDL	11.0	<MDL	134.8	8.6	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	2.0	<MDL	<MDL	<MDL	22.8	5.0	<MDL	<MDL	<MDL	<MDL
3	MO River	Chloramines	Untreated	<MDL	1.9	<MDL	4.6	<MDL	27.6	4.4	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	4.0	<MDL	12.4	1.5	<MDL	<MDL	<MDL	<MDL
4	Alluvial GW	Chloramines	Untreated	<MDL	1.3	<MDL	4.8	<MDL	32.4	8.3	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	1.3	<MDL	8.8	3.4	<MDL	<MDL	<MDL	<MDL
5	Alluvial GW	Free chlorine	Untreated	<MDL	<MDL	<MDL	3.9	<MDL	7.2	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	7.2	<MDL	<MDL	<MDL	<MDL	<MDL
6	Deep rock wells	Chloramines	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	18.4	1.3	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	20.9	<MDL	<MDL	<MDL	<MDL	<MDL
7	Deep rock wells	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	14.1	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	6.1	<MDL	<MDL	<MDL	<MDL	<MDL
8	Reservoirs	Free chlorine	Untreated	<MDL	3.0	<MDL	<MDL	<MDL	56.0	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	17.8	<MDL	<MDL	<MDL	<MDL	<MDL
9	Reservoir	Chloramines	Untreated	<MDL	1.3	<MDL	<MDL	<MDL	6.6	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	3.2	<MDL	<MDL	<MDL	<MDL	<MDL
10	MO River	Chloramines	Untreated	<MDL	<MDL	<MDL	20.3	9.4	46.0	7.3	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	1.6	6.2	35.6	5.0	<MDL	<MDL	<MDL	<MDL

ND = No Data

MDL = Method Detection Limit

Table 5. (continued)

ID #	Water source	Treatment	Sample type	Concentration (ng/L)										
				Tylo-sin	Linco-myacin	Trimetho-prim	Sulfameth-oxazole	Acetamin-ophen	Caf-feine	Carbamaz-epine	Ced-cine	Triclo-san	Ibu-pro-fen	Ioprom-ide
11	MS River	Free chlorine	Untreated	<MDL	3.9	<MDL	4.0	46.0	25.3	4.2	<MDL	7.0	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	9.5	11.6	1.2	<MDL	<MDL	<MDL	<MDL
12	Lake	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	32.8	59.6	<MDL	<MDL	2.9	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	9.4	16.4	<MDL	<MDL	2.2	<MDL	<MDL
13	Lake	Chloramines	Untreated	<MDL	<MDL	<MDL	1.9	<MDL	6.0	<MDL	<MDL	4.1	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	3.3	<MDL	<MDL	2.6	<MDL	<MDL
14	Lake	Chloramines	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	75.6	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	14.6	<MDL	<MDL	<MDL	<MDL	<MDL
15	Deep Well	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	1.7	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	1.4	<MDL	<MDL	<MDL	<MDL	<MDL
16	Deep Well	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	1.6	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	1.4	<MDL	<MDL	<MDL	<MDL	<MDL
17	Deep Well	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	14.9	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	6.5	<MDL	<MDL	<MDL	<MDL	<MDL
18	Deep Well	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	14.5	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	6.3	<MDL	<MDL	<MDL	<MDL	<MDL
19	Lake	Free chlorine	Untreated	<MDL	<MDL	<MDL	1.1	<MDL	16.4	1.6	<MDL	3.8	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	14.9	<MDL	<MDL	3.5	<MDL	<MDL
20	Unconsolidated Wells	Free chlorine	Untreated	3.9	7.0	5.1	3.2	<MDL	13.2	9.6	<MDL	3.1	<MDL	<MDL
			Treated	<MDL	4.4	4.7	1.5	<MDL	8.1	6.9	<MDL	2.6	<MDL	<MDL

ND = No Data

MDL = Method Detection Limit

Table 5. (continued)

ID #	Water source	Treatment	Sample type	Concentration (ng/l)										
				Tylo-sin	Linco-myoin	Trimetho-prin	Sulfameth-oxazole	Acetamin-ophen	Caf-feine	Carbama-zepine	Cod-eine	Triclo-san	Ibu-pro-fen	Ioprom-ide
21	Unconsolidated Wells	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	5.2	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	1.5	<MDL	<MDL	<MDL	<MDL	<MDL
22	Unconsolidated Wells	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	152.0	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	1.2	<MDL	<MDL	<MDL	<MDL	<MDL
23	Unconsolidated Wells	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	111.2	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	9.6	1.3	<MDL	<MDL	<MDL	<MDL
24	Lake	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	8.9	<MDL	<MDL	5.0	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	2.7	<MDL	<MDL	4.9	<MDL	<MDL
25	Lake	Chloramines	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	24.0	<MDL	<MDL	4.4	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	4.4	<MDL	<MDL	4.2	<MDL	<MDL
26	Lake	Free chlorine	Untreated	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	5.8	<MDL	<MDL	7.3	<MDL	<MDL
27	Reservoir	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	12.4	7.6	<MDL	5.2	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	11.1	4.7	<MDL	3.4	<MDL	<MDL
28	Lake	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	41.2	<MDL	<MDL	9.1	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	6.8	<MDL	<MDL	5.4	<MDL	<MDL
29	River	Chloramines	Untreated	<MDL	<MDL	<MDL	<MDL	4.6	13.1	17.9	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	10.6	3.6	<MDL	<MDL	<MDL	<MDL
30	Lake	Free chlorine	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	8.9	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	2.5	<MDL	<MDL	<MDL	<MDL	<MDL
31	Lake	Chloramines	Untreated	<MDL	<MDL	<MDL	<MDL	<MDL	6.4	<MDL	<MDL	<MDL	<MDL	<MDL
			Treated	<MDL	<MDL	<MDL	<MDL	<MDL	3.6	<MDL	<MDL	<MDL	<MDL	<MDL

ND = No Data

MDL = Method Detection Limit

Table 6. Seasonal monitoring of PPCPs from February to June 2009.

Month	Water source	Treatment	Sample type	Concentration (ng/L)							
				Linco- mycin	Trimetho- prim	Sulfameth- oxazole	Acetamin- ophen	Caf- feine	Carbama- zepine	Triclo- san	Ibupro- fen
Feb	MO River	Free chlorine	Untreated	1.8	2.8	18.8	16.0	49.6	5.5	2.1	27.1
	"	"	Treated	<MDL	<MDL	8.2	<MDL	36.0	4.7	<MDL	23.4
	Reservoir	Chloramines	Untreated	2.5	<MDL	<MDL	14.2	157.2	1.0	<MDL	2.4
	"	"	Treated	<MDL	<MDL	<MDL	<MDL	18.4	<MDL	<MDL	<MDL
	MS River	Chloramines	Untreated	4.2	4.6	13.7	5.3	47.2	8.4	<MDL	16.6
	"	"	Treated	<MDL	<MDL	<MDL	<MDL	13.0	2.2	<MDL	8.8
April	MO River	Chloramines	Untreated	1.1	<MDL	14.0	<MDL	38.3	4.2	<MDL	2.2
	"	"	Treated	<MDL	<MDL	6.8	<MDL	22.0	2.1	<MDL	<MDL
	Reservoir	Free chlorine	Untreated	5.9	<MDL	2.2	<MDL	110.8	1.3	<MDL	<MDL
	"	"	Treated	<MDL	<MDL	<MDL	<MDL	2.7	<MDL	<MDL	<MDL
	MS River	Chloramines	Untreated	1.8	2.6	9.4	<MDL	19.9	4.6	4.2	<MDL
	"	"	Treated	<MDL	<MDL	<MDL	<MDL	3.4	<MDL	3.4	<MDL
May	MO River	Free chlorine	Untreated	2.3	<MDL	8.4	<MDL	17.6	3.3	5.4	<MDL
	"	"	Treated	<MDL	<MDL	5.6	<MDL	10.6	<MDL	<MDL	<MDL
	Reservoir	Free chlorine	Untreated	6.9	<MDL	2.2	<MDL	4.6	1.1	8.1	<MDL
	"	"	Treated	<MDL	<MDL	<MDL	<MDL	3.7	<MDL	<MDL	<MDL
	MS River	Chloramines	Untreated	2.0	<MDL	6.7	<MDL	18.7	4.0	8.9	<MDL
	"	"	Treated	<MDL	<MDL	<MDL	<MDL	2.8	<MDL	6.9	<MDL
June	MO River	Chloramines	Untreated	1.9	<MDL	4.6	<MDL	27.6	4.4	<MDL	<MDL
	"	"	Treated	<MDL	<MDL	4.0	<MDL	12.4	1.5	<MDL	<MDL
	Reservoir	Free chlorine	Untreated	1.3	<MDL	<MDL	<MDL	6.6	<MDL	<MDL	<MDL
	"	"	Treated	<MDL	<MDL	<MDL	<MDL	4.0	<MDL	<MDL	<MDL
	MS River	Free chlorine	Untreated	2.6	<MDL	4.2	<MDL	15.6	5.7	3.1	<MDL
	"	"	Treated	<MDL	<MDL	<MDL	<MDL	9.5	1.0	<MDL	<MDL

MDL = Method Detection Limit

found that the oxidation of erythromycin and acetaminophen by free chlorine were a little faster at pH 8.6 than pH 6.6. Most pharmaceuticals can be removed at the CT value of 200 mg·min/L at both pHs.

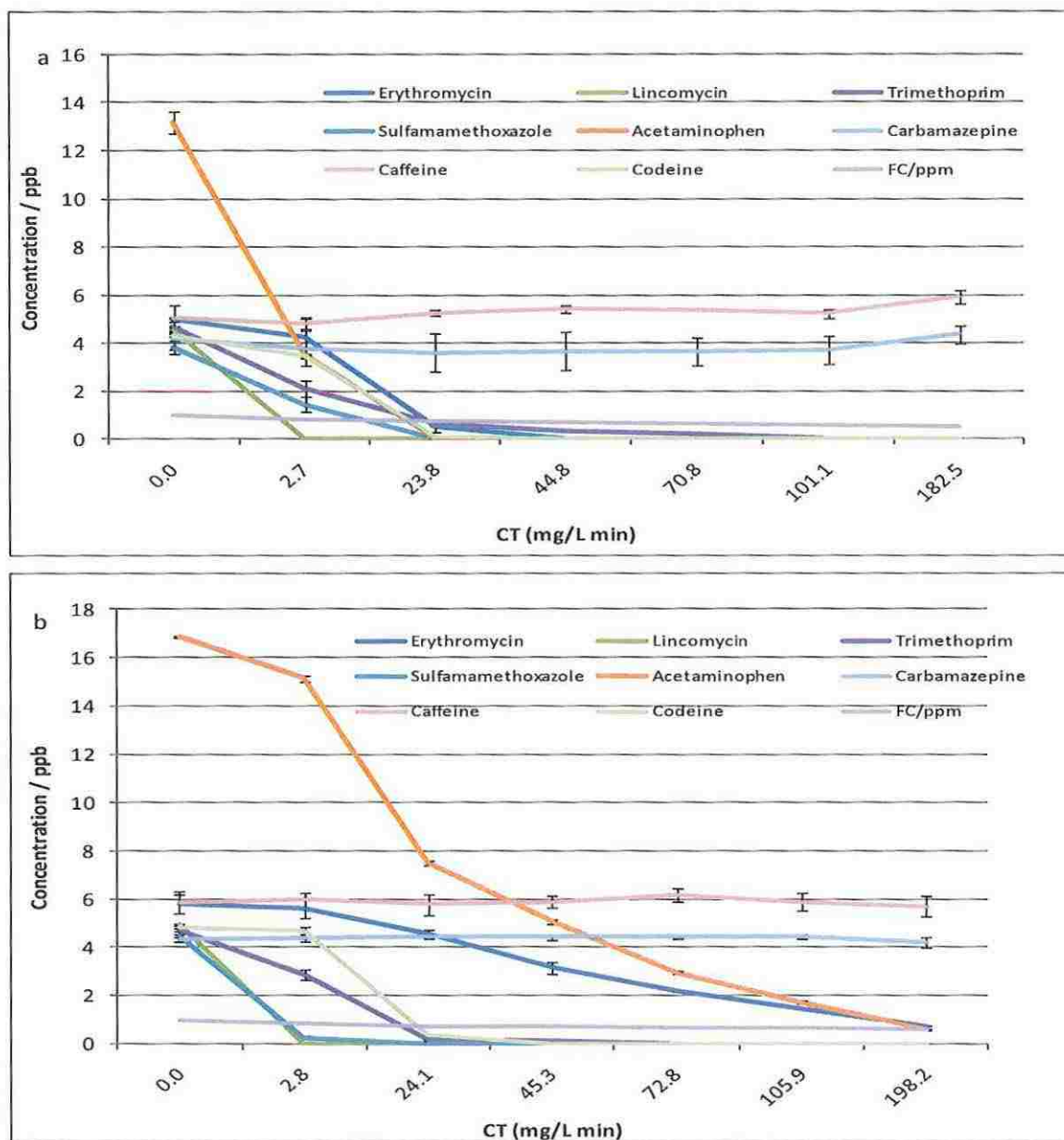


Figure 1. The oxidation of selected pharmaceutical compounds by free chlorine in (a) pH 8.6 buffer and (b) pH 6.6 buffer.

The removal experiments were also carried out in the lake water for comparison (Figure 2). The concentration of free chlorine decreased faster in real water oxidation than lab DI water. This indicated that the real water matrix had a strong competition with the selected pharmaceutical compounds for free chlorine oxidant. Most pharmaceuticals can still be removed during the oxidation study, but the rate was much slower than that in the lab DI water. The results showed that the oxidation trends for all of the studied pharmaceutical compounds in lake water were the same as those in the lab DI water.

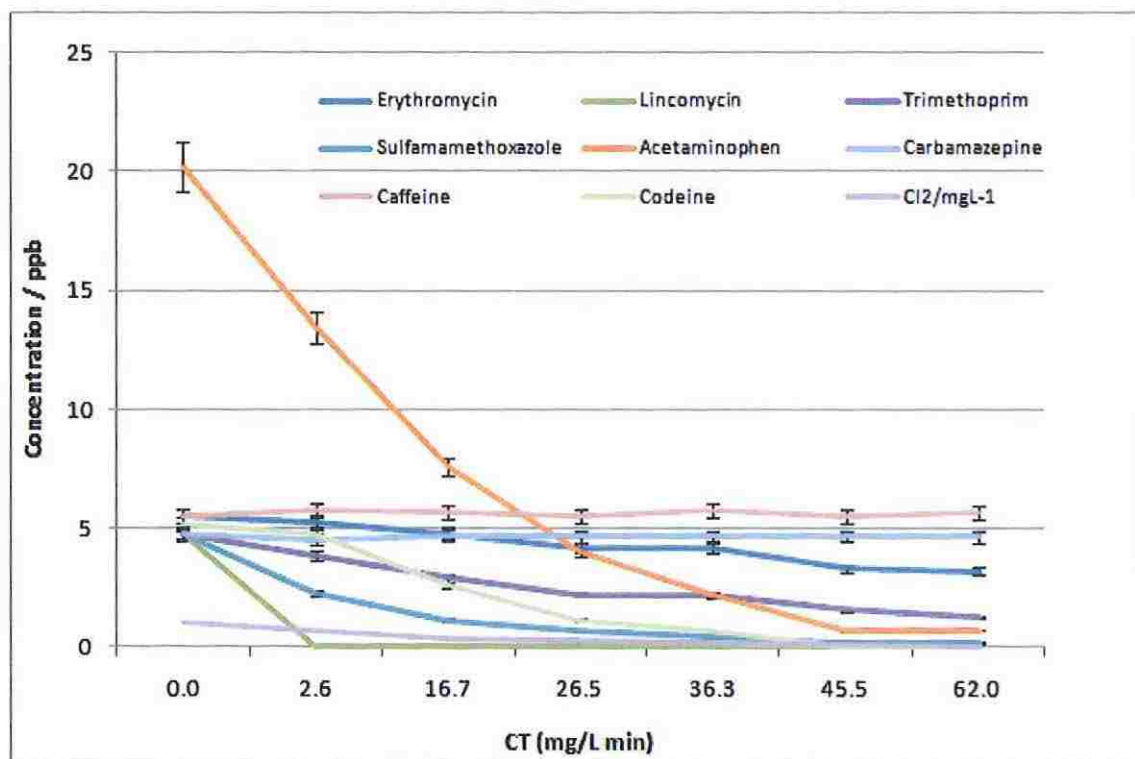


Figure 2. The concentration of detected pharmaceutical compounds in free chlorine oxidation experiment in pH 8.6 lake water.

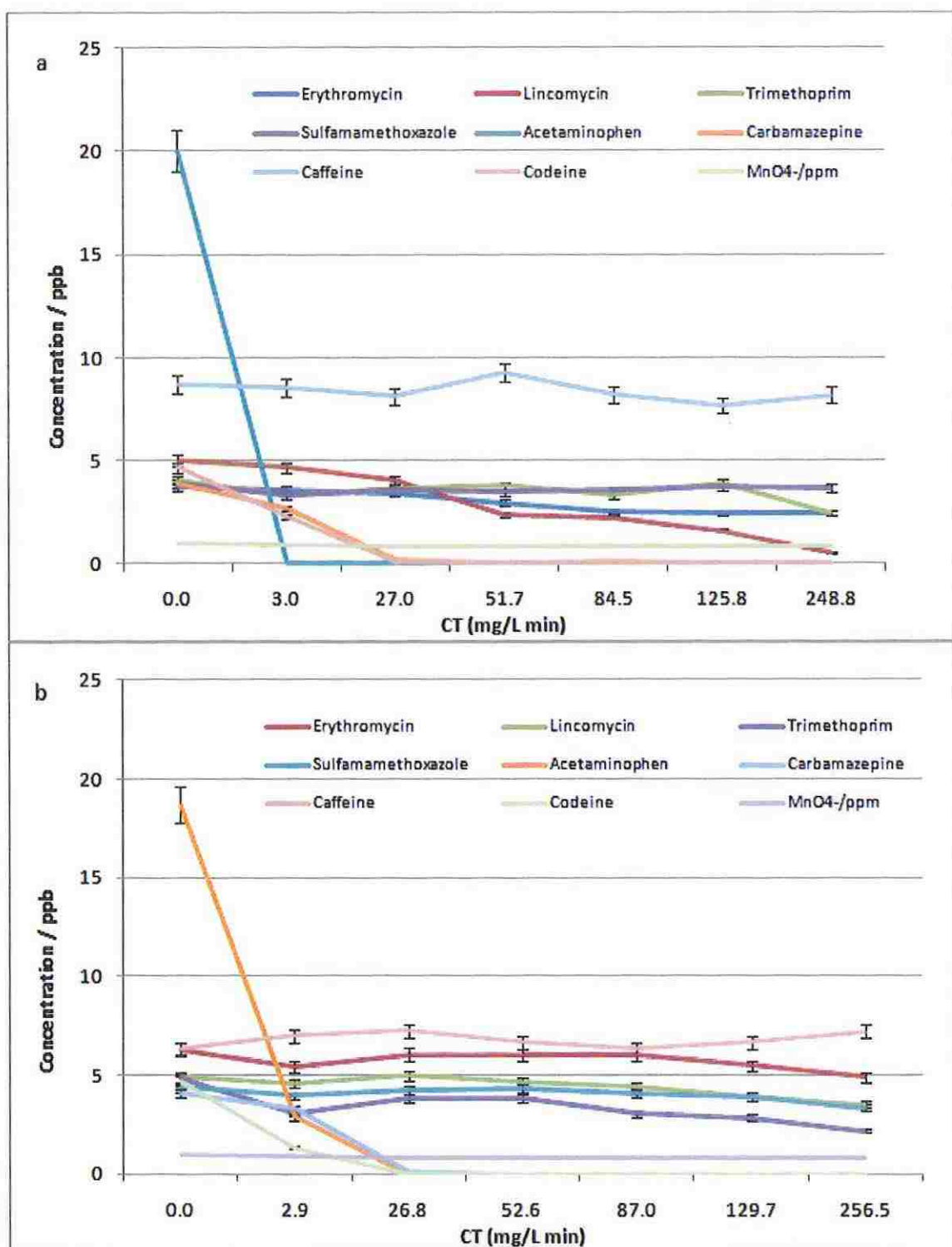


Figure 3. The oxidation of selected pharmaceutical compounds by permanganate in (a) pH 8.6 buffer and (b) pH 6.6 buffer.

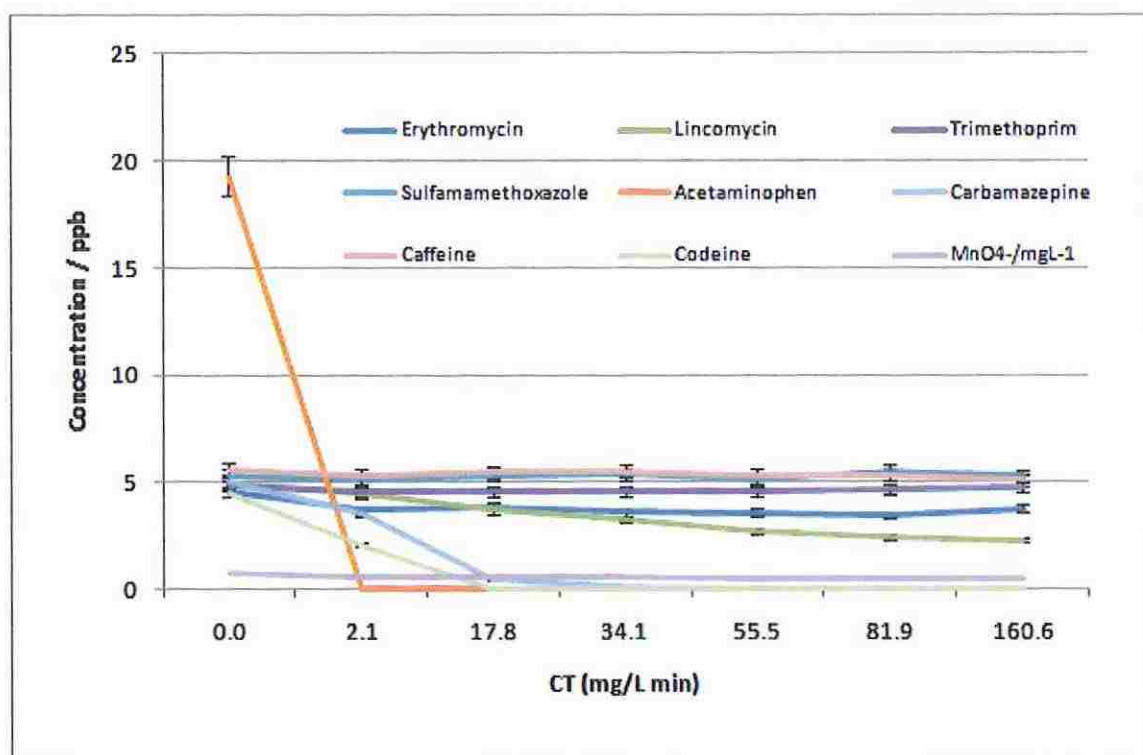


Figure 4. The oxidation of selected pharmaceutical compounds by permanganate in pH 8.6 Missouri river water.

3.3 Ozone oxidation

The reactivity of selected compounds with ozone (1.5 mg/L) in two different pH buffer systems was shown in Figure 5. The oxidation of the selected pharmaceuticals by ozone was quite rapid and completed in about 2 min. In addition, ozone was unstable in aqueous solution. Due to these two reasons, the concentration of ozone was barely detected after 2 min. As a result, a CT curve was not used in the ozone oxidation studies. The concentration of each pharmaceutical compound did not decrease significantly after two minutes, which indicated that the soluble ozone in the oxidation system was entirely

limit after 2 min., while the experiment in the literature reported 0.2-0.3 mg/L of ozone after 3 min (Snyder et al. 2006; Westerhoff et al. 2005).

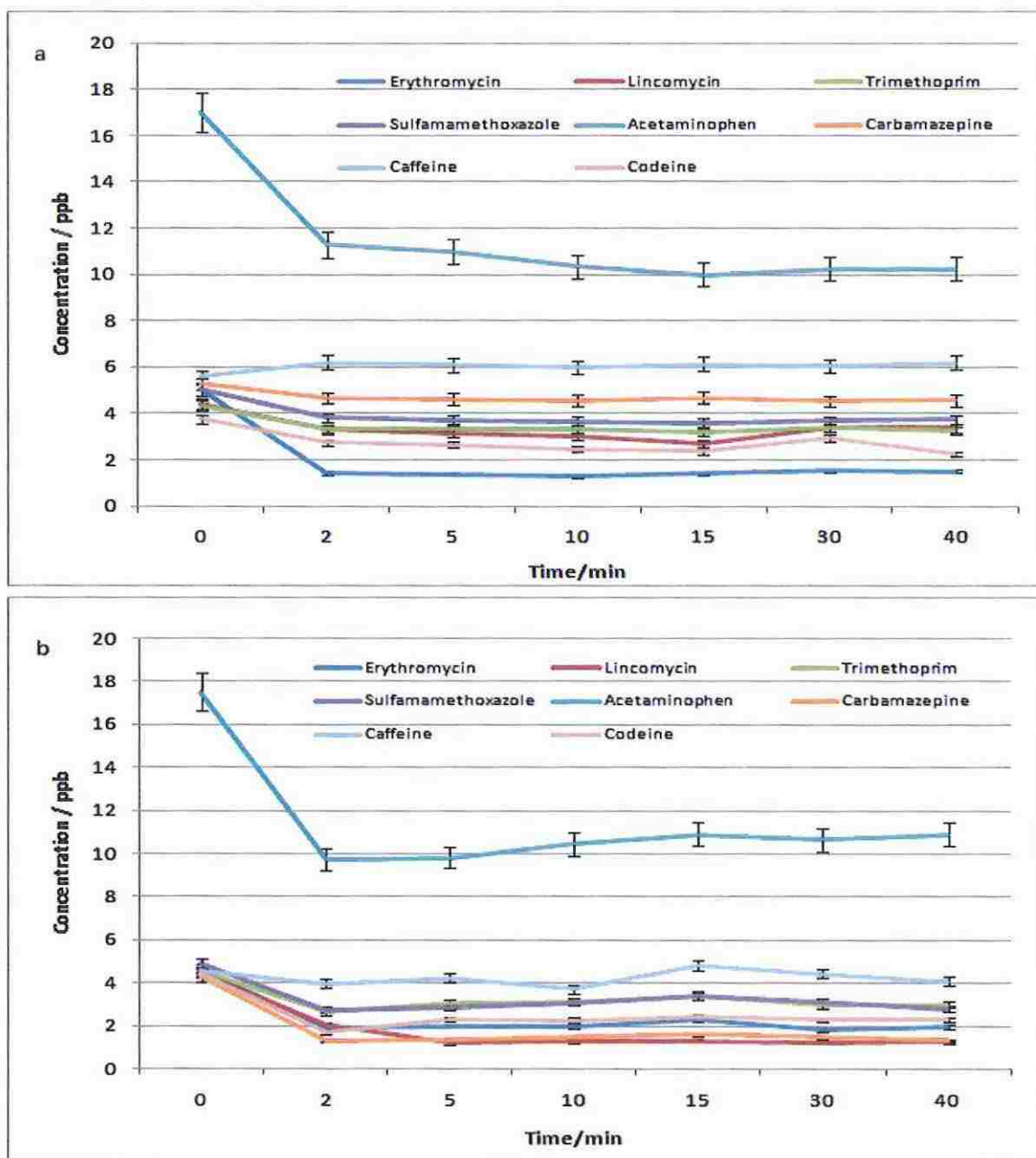


Figure 5. The oxidation of selected pharmaceutical compounds by ozone in (a) pH 8.6 buffer and (b) pH 6.6 buffer.

and all other pharmaceuticals showed about 20-30% removal at the selected conditions. No obvious difference in the removal efficiency was found at different pHs.

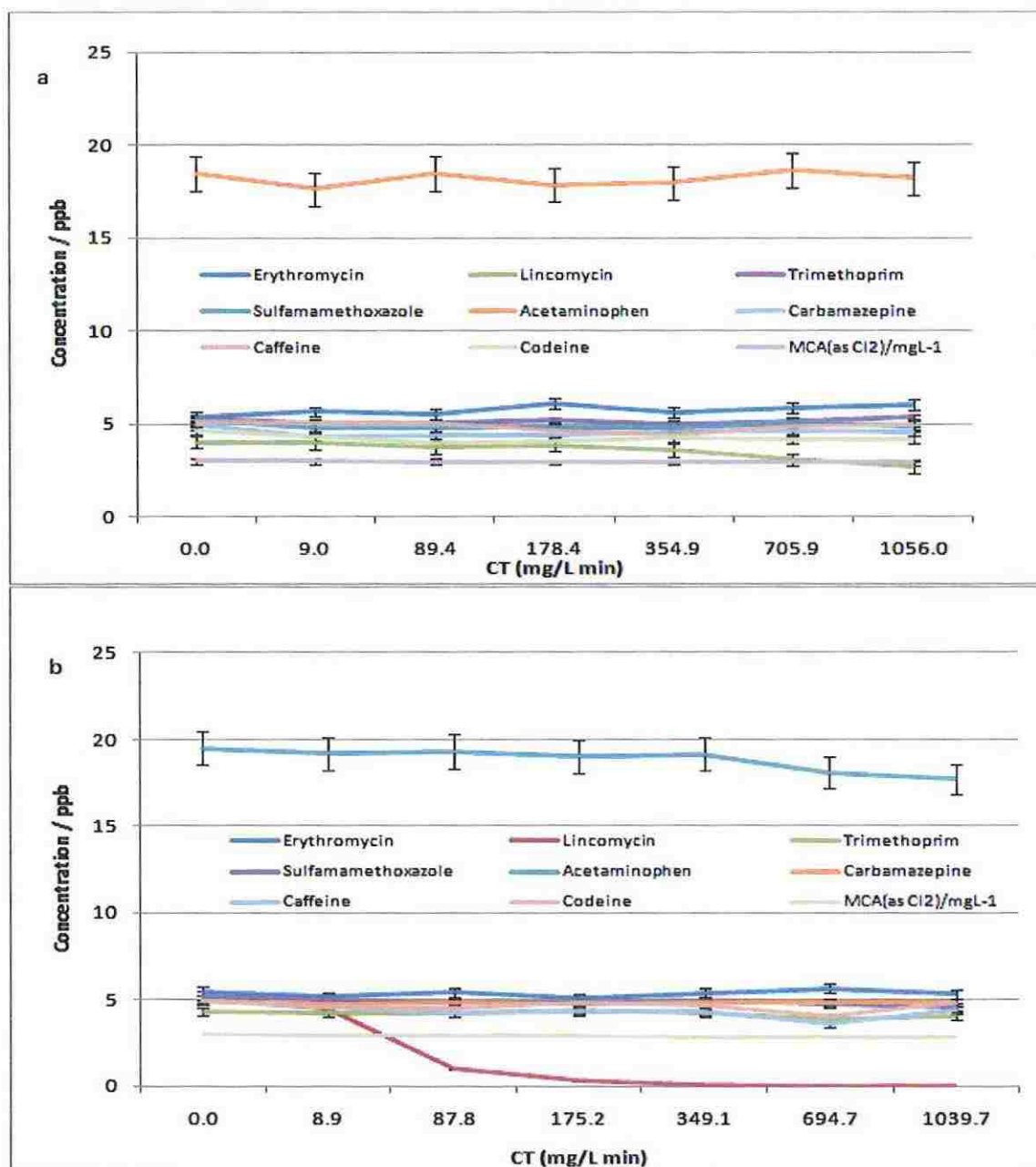


Figure 6. The oxidation of selected pharmaceutical compounds by monochloramine in (a) pH 8.6 buffer and (b) pH 6.6 buffer.

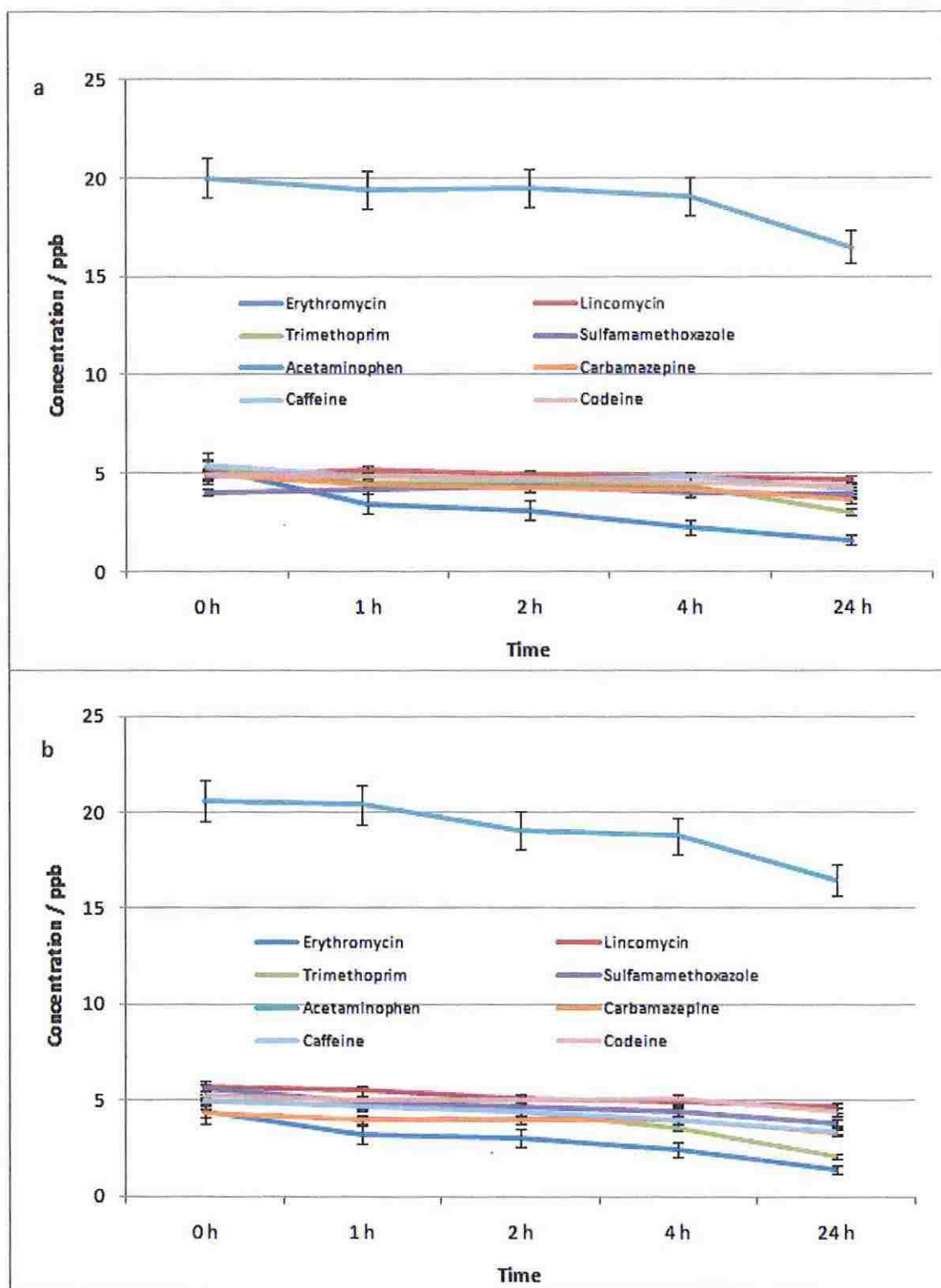


Figure 7. The concentration of detected pharmaceutical compounds in PAC removal experiment in (a) pH 8.6 buffer and (b) pH 6.6 buffer.

The PAC removal experiment was also carried out in Missouri River water to investigate the effect of sample matrices (Figure 8). The data showed that most pharmaceuticals were not removed from the river water at the selected dosage of PAC even when the equilibrium was reached. This comparison indicated that the sample matrix played an important role in the pharmaceutical removal in natural surface water.

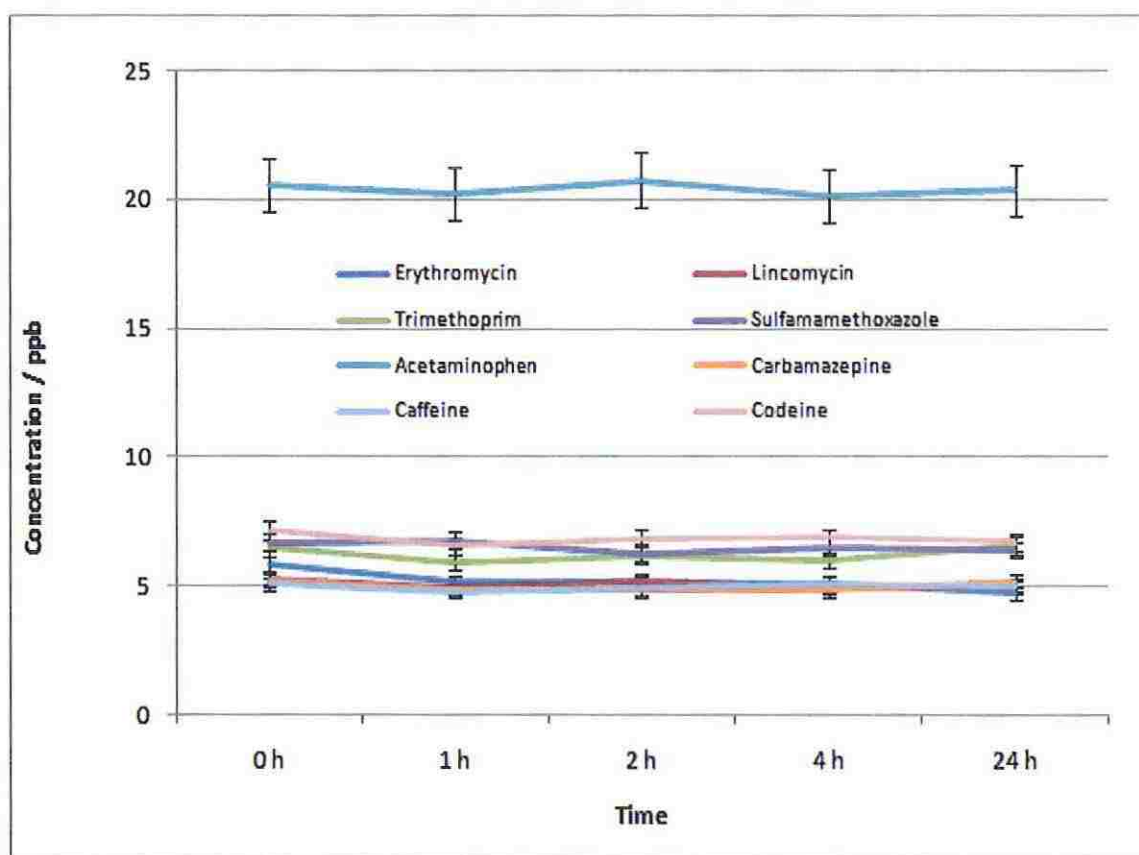
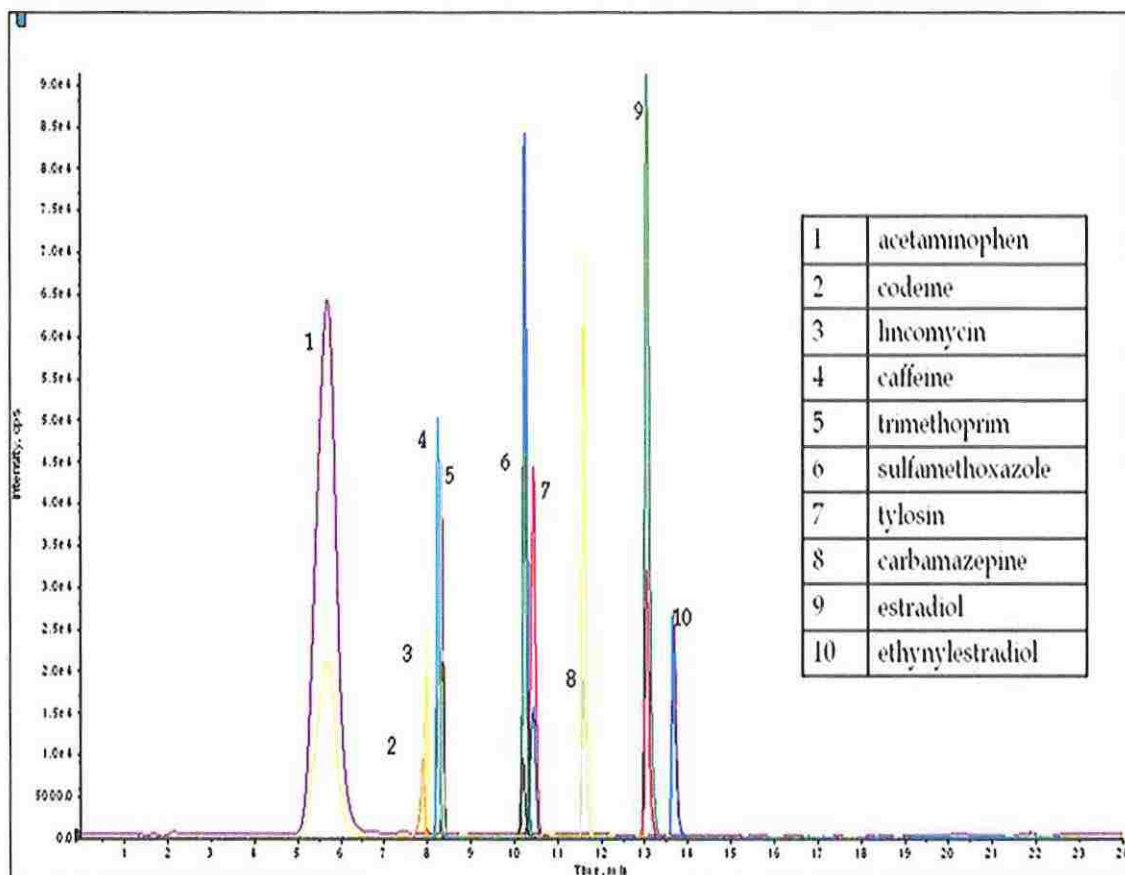
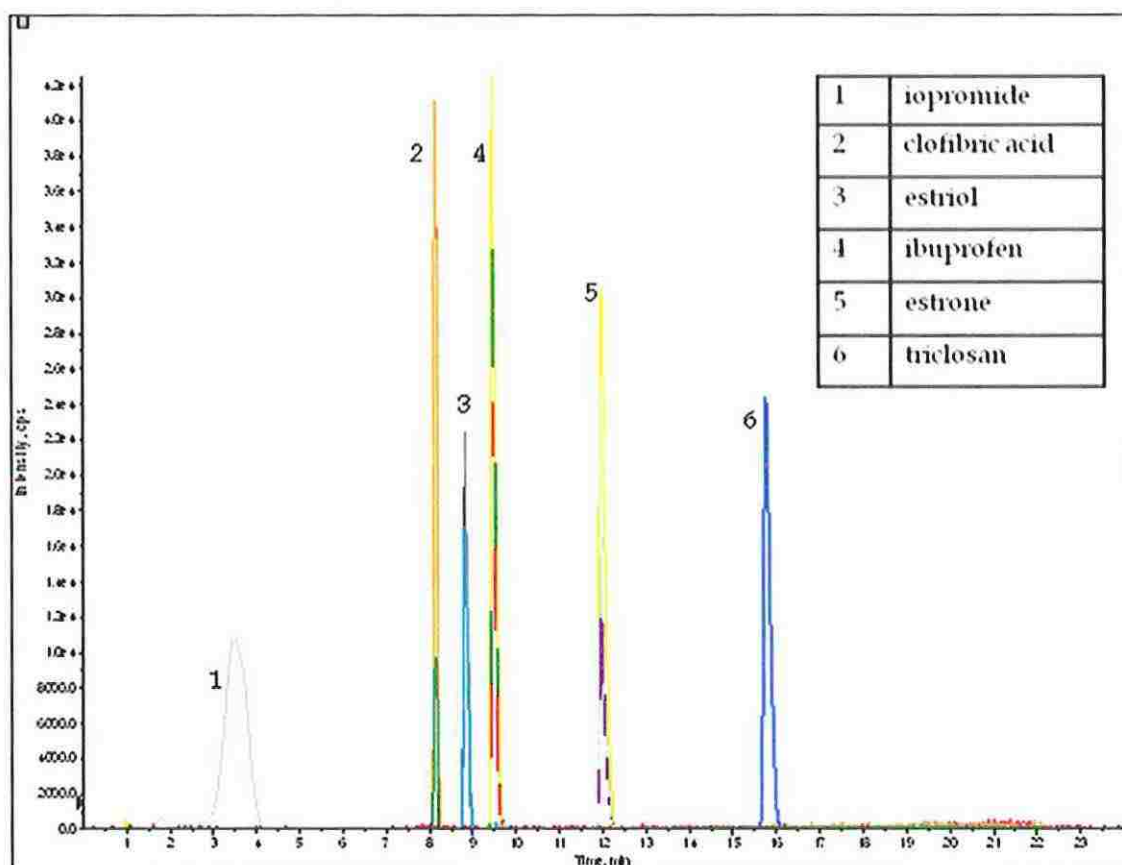


Figure 8. The concentration of detected pharmaceutical compounds in PAC removal experiment in pH 8.6 Missouri river water matrix.

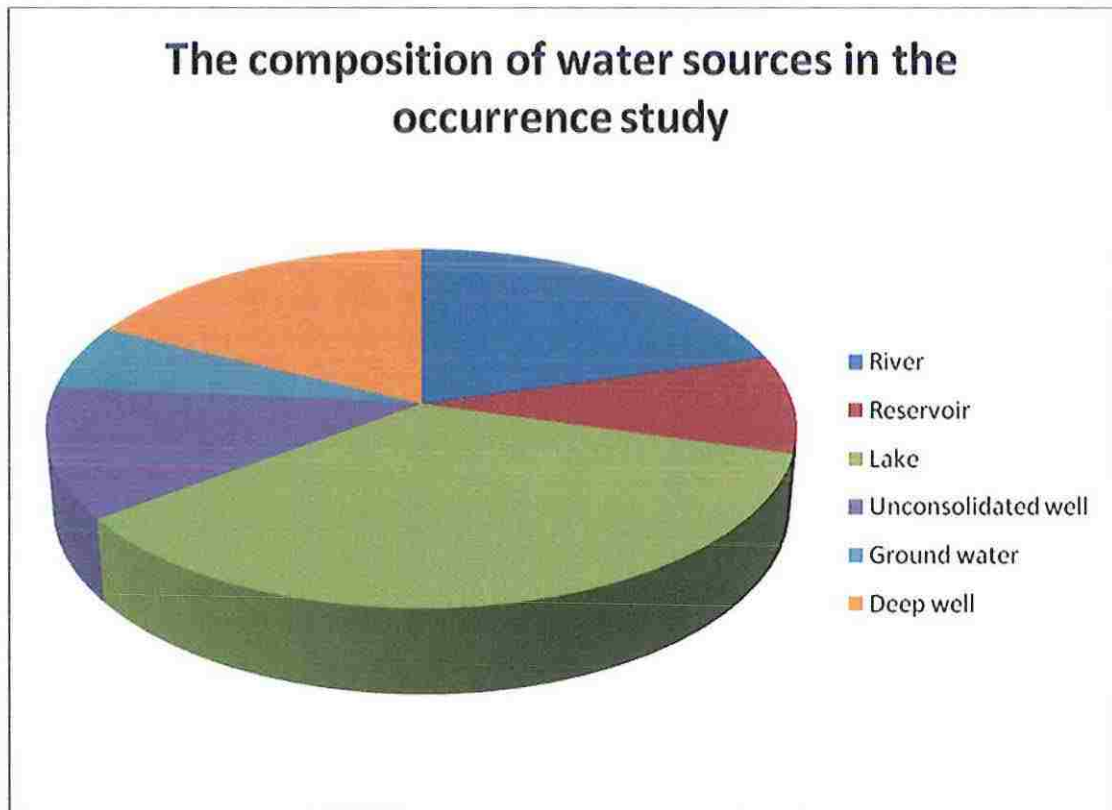
Total ion chromatogram of pharmaceutical compounds in positive ionization mode:



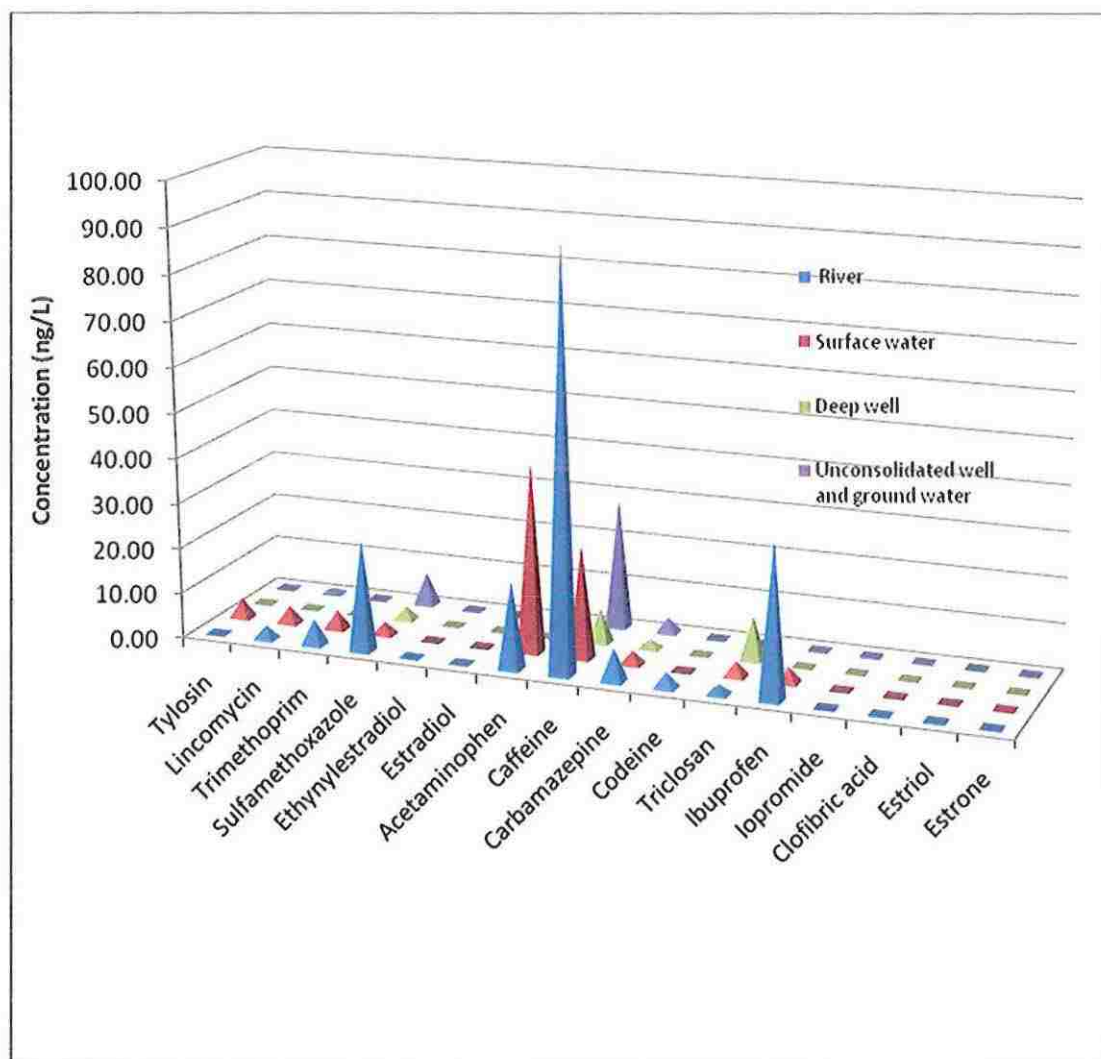
Total ion chromatogram of pharmaceutical compounds in negative ionization mode.



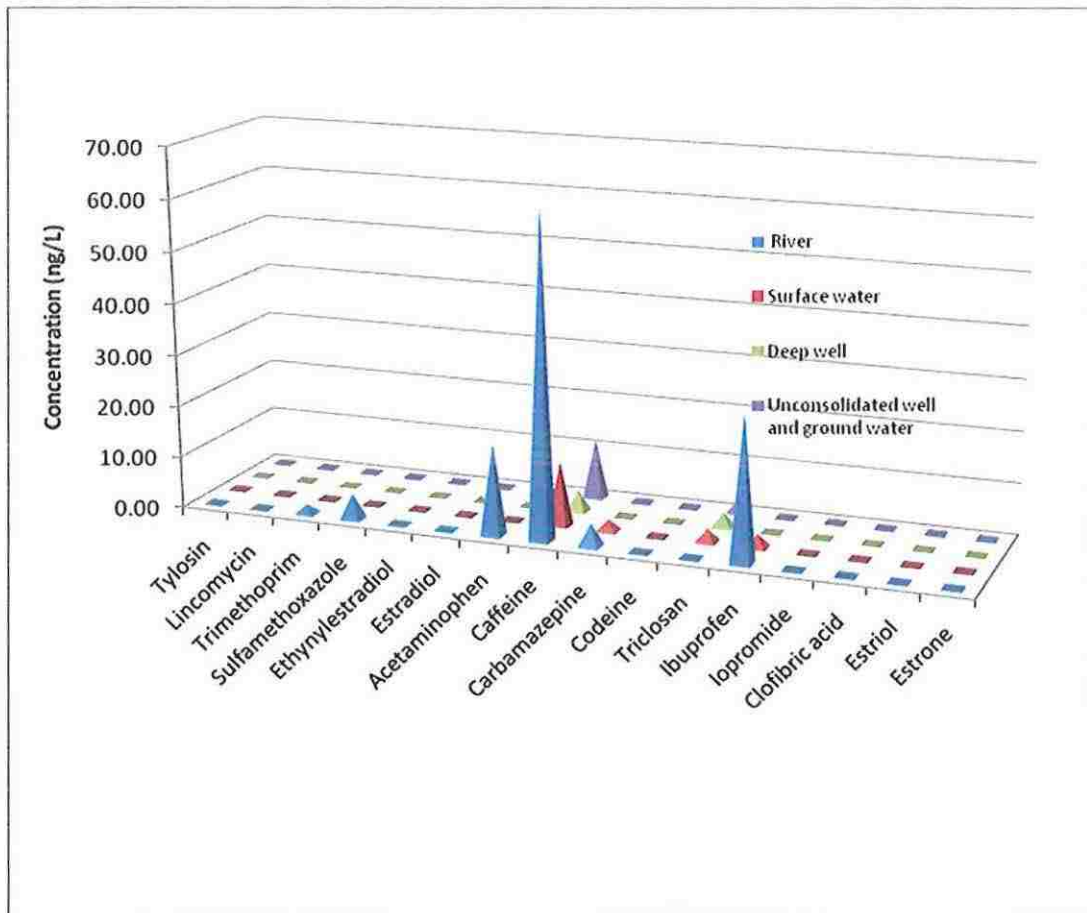
The composition of water sources in the occurrence study.



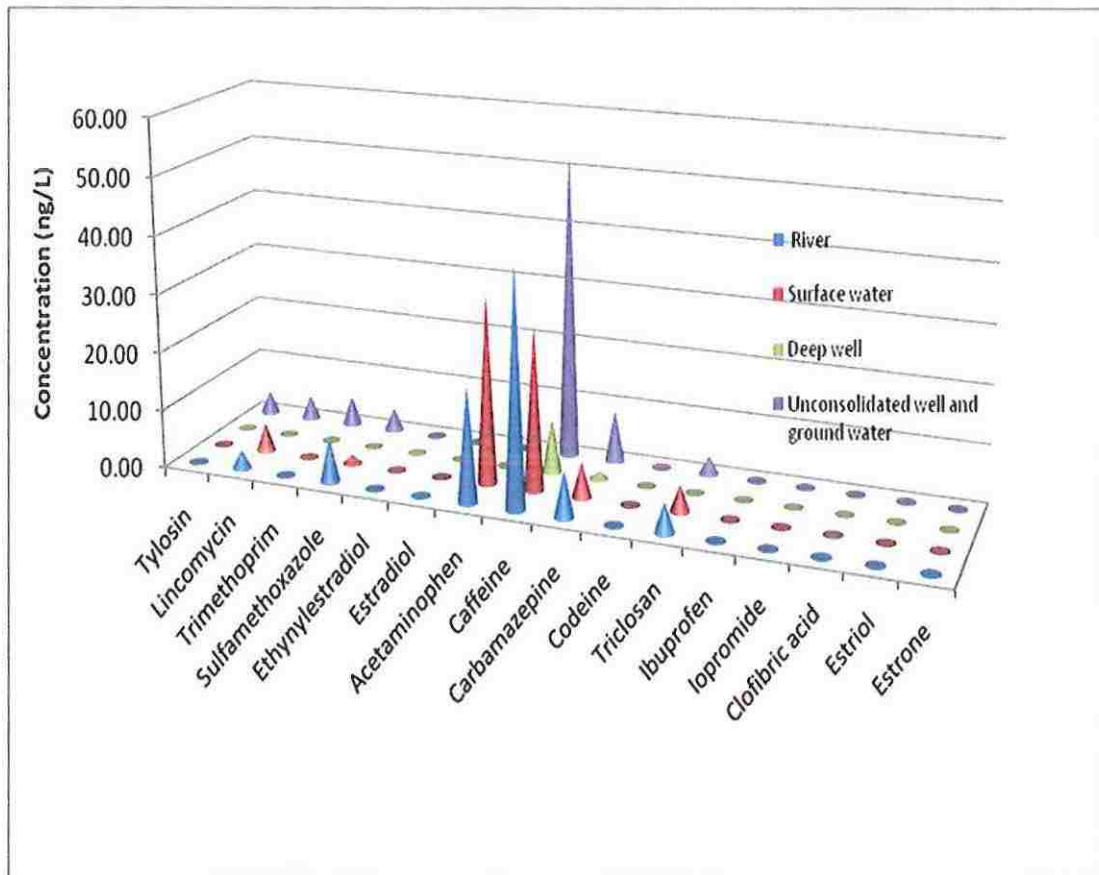
The pharmaceuticals levels in untreated water samples (ng/L). (Winter)



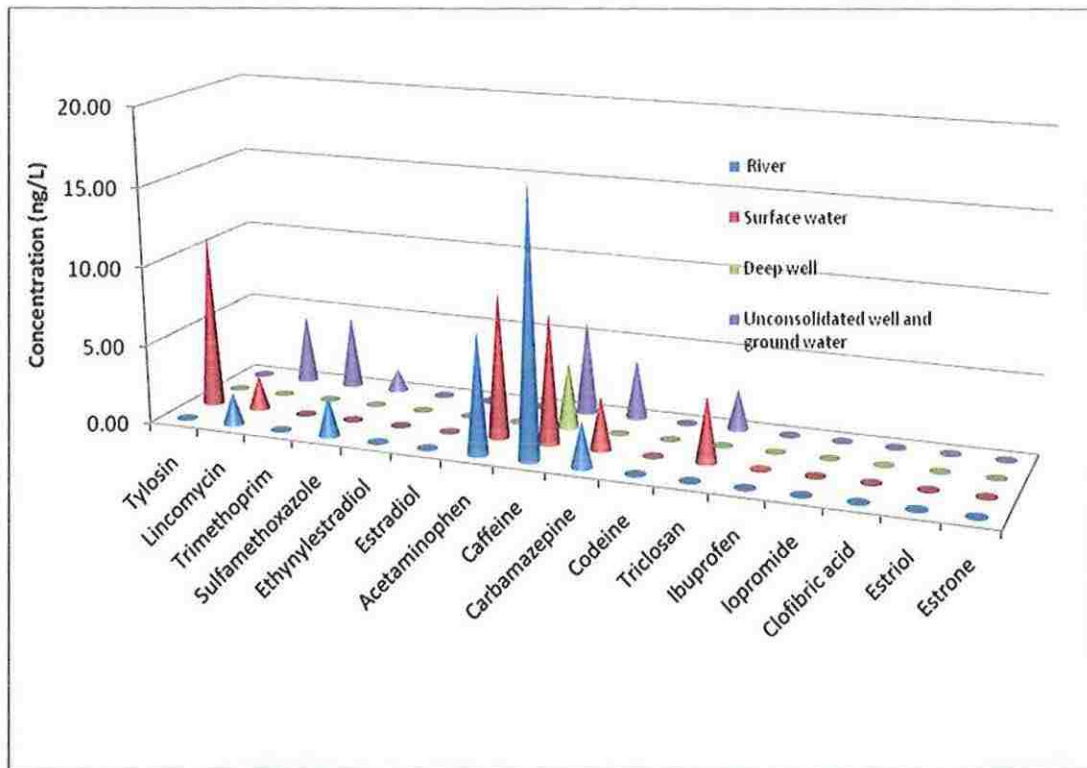
The pharmaceuticals levels in treated water samples (ng/L). (Winter)



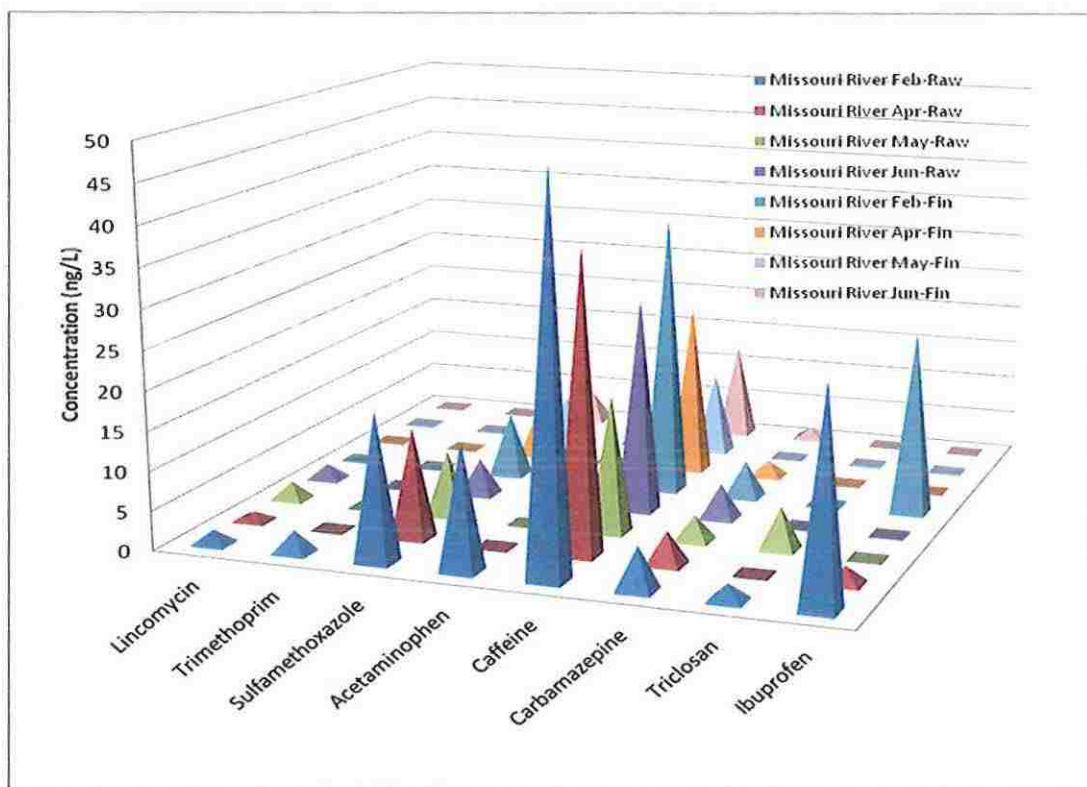
The pharmaceuticals levels in untreated water samples (ng/L). (Summer)



The pharmaceuticals levels in treated water samples (ng/L). (Summer)



The pharmaceuticals levels in Missouri river from February to June 2009 (ng/L).



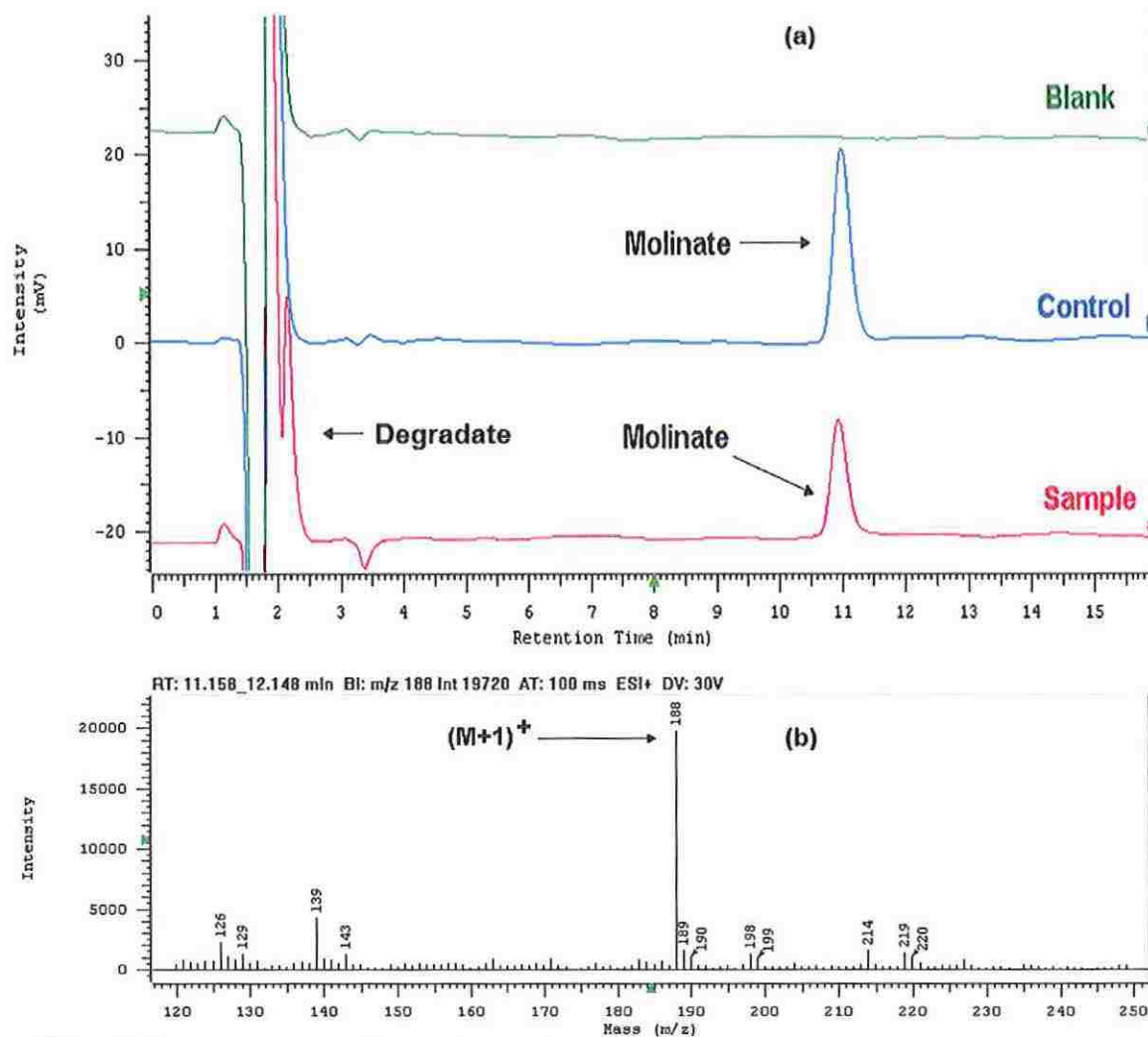


Figure 1. (a) LC-UV chromatograms of blank, control (standard molinate), and oxidation degradate of molinate under chromatographic condition 1. (b) Mass spectrum of the molinate standard (MW: 187).

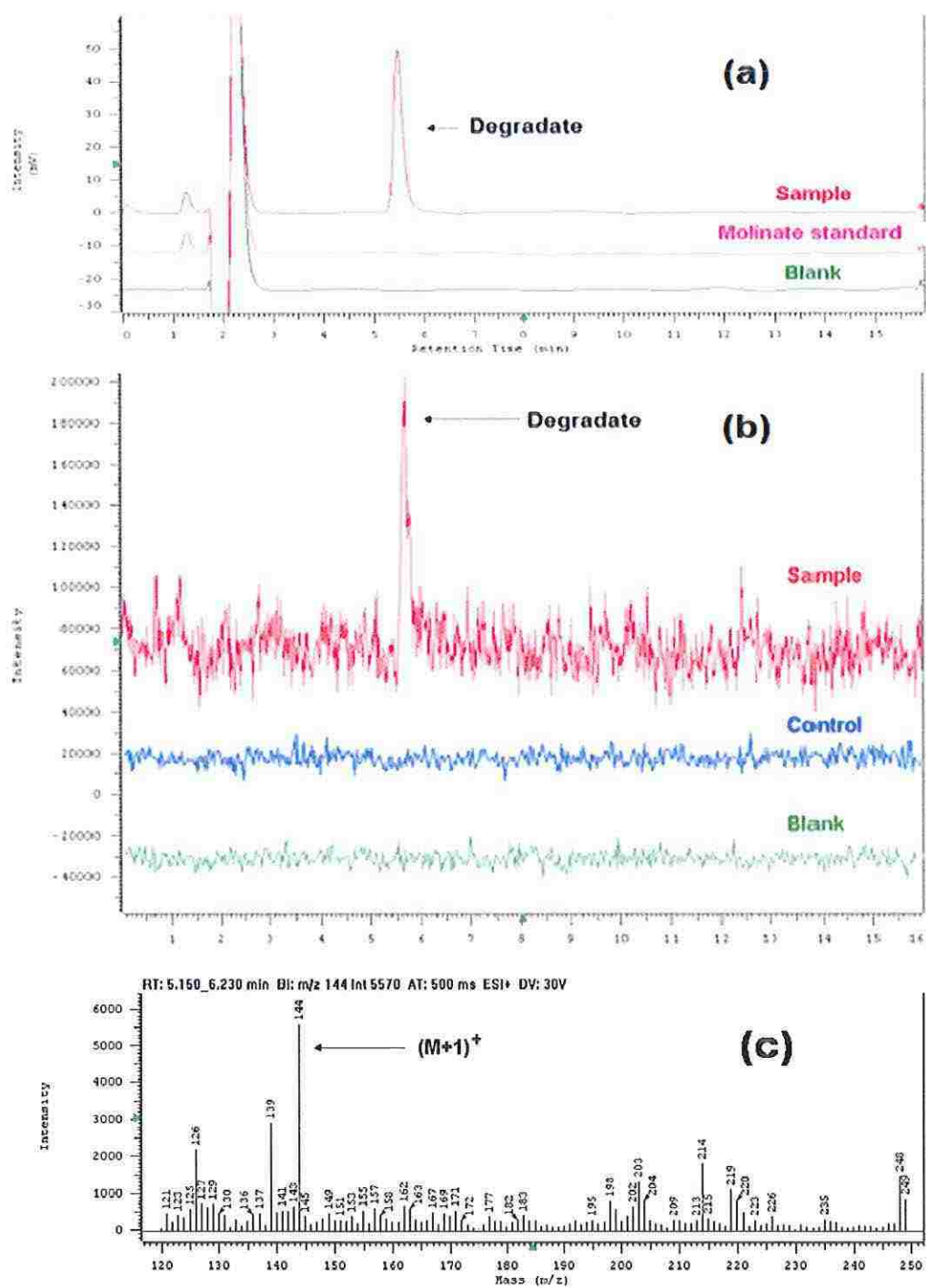


Figure 2. (a) LC-UV chromatograms of blank, control (standard molinate), and oxidation degradate of molinate under chromatographic condition 2. (b) Total ion chromatograms of blank, control (standard molinate) and oxidation degradate of molinate under chromatographic condition 2. (c) Mass spectrum for oxidation degradate of molinate by free chlorine and ozone.

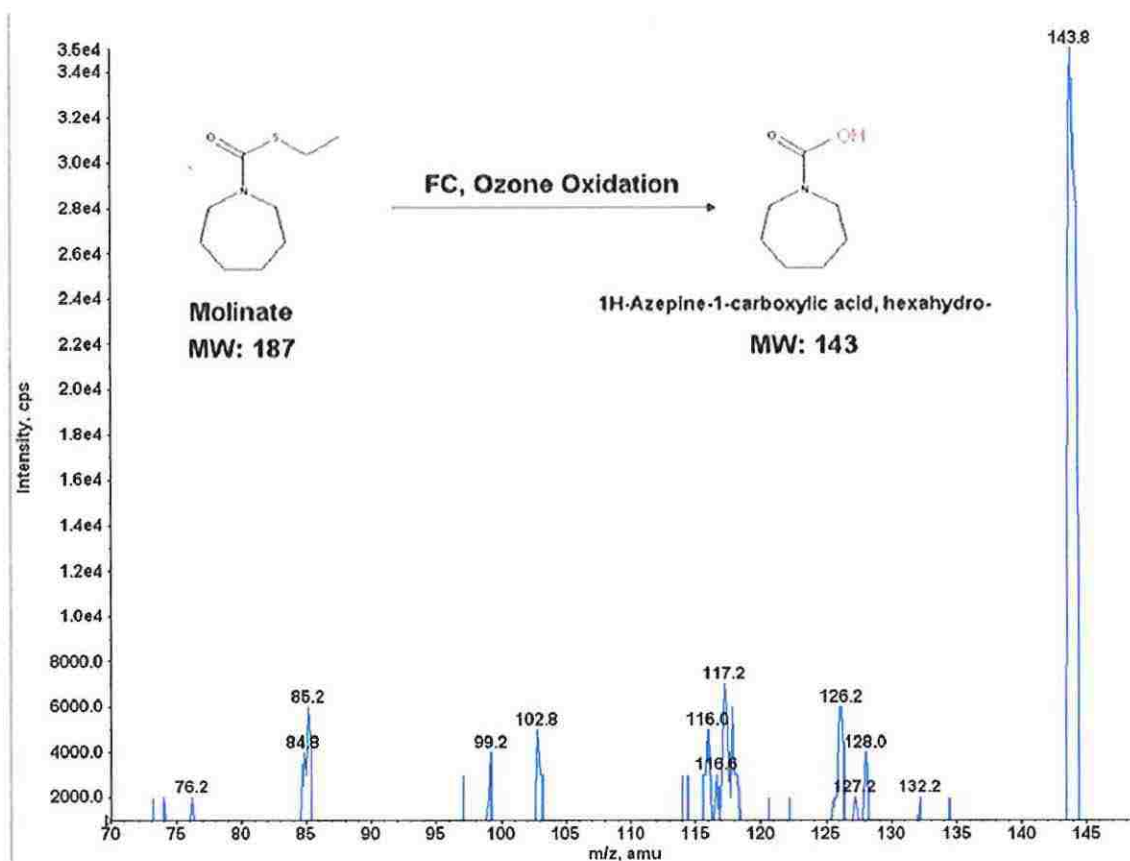


Figure 3. (a) Mass spectrum of the degradation product of molinate by using API 4000 triple quadrupole mass spectrometer. (b) Product ion scans of the degradation product using API 4000 triple quadrupole mass spectrometer.

Quantitative results of the oxidation of molinate using several oxidation systems.

The quantitative studies depicted in Table 1 show that the percentage of molinate removed by various oxidants had changed significantly. The data demonstrated that molinate can only be oxidized by free chlorine and ozone, while other oxidants do not show significant removal (7%). The reaction of molinate with free chlorine was quite fast; 10 mg L⁻¹ of molinate were totally removed by 10 mg L⁻¹ of free chlorine within two hours. UV

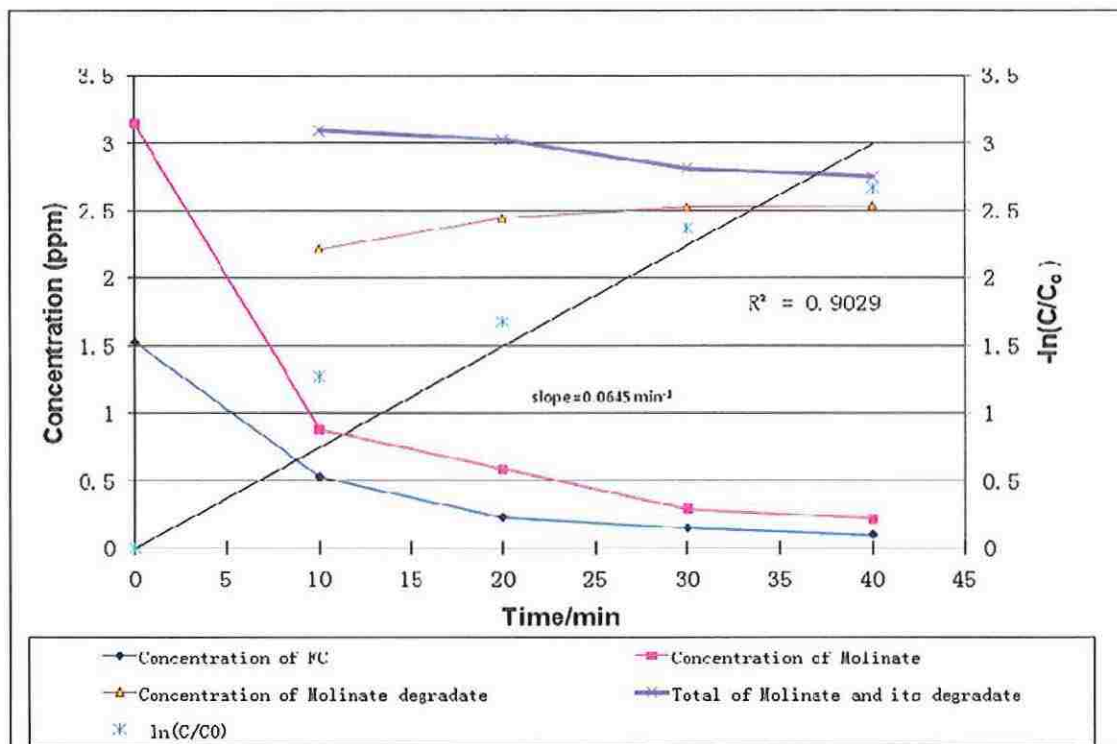


Figure 4. Concentration-Time curve for FC oxidation of molinate.

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