

Supplementary Material

Contaminant of Emerging Concerns in Modder River Catchment of Free State: Implication for Environmental Risk and Water Sources Protection

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Table S1. Sampling points in the Modder River catchment.

Item	Sample ID	Coordinates			Site description
		Latitude	Longitude	Elevation	
Surface water (Dams)					
1	SWMSO1	29°01'4.9" S	26°24'2.7" E	1344 m	It serve as a resort and conference centre with few houses around.
2	SWMD02	29°02'8.4" S	26°27'5.8" E	1354 m	It also serve as a resort. Surrounded by farm houses.
3	SWKD08	28°53'03" S	25°57'21" E	1226 m	Few houses, fishing activities and some agricultural fields.
4	SWSD09	29°12'10" S	26°47'38" E	1460 m	Approximately 1 km away from residential area. Household waste is dumped nearby.
5	SWRUSD10	29°16'20" S	26°37'00" E	1370 m	Around agricultural areas. Some few houses near the dam.
Surface water (Rivers)					
6	SWRS03	29°06'9.6" S	26°19'7.2" E	1379 m	Intense agricultural activities within 500 m range.
7	SWBS04	29°07'2.4" S	26°17'1.5" E	1390 m	It is close to wastewater treatment work. Bisect residential and industrial areas
8	SWKOR05	29°12'8.3" S	26°31'0.4" E	1334 m	Around agricultural activities, farm houses and old mechanical work shop.
9	SWMOR06	29°09'39.3" S	26°34'20.3" E	1327 m	Near a national road and railway line.
10	SWKLM07	29°14'34.3" S	26°40'26.2" E	1373 m	It passes through a township, receives wastewater effluent, and polluted by domestic wastes.
Treated drinking water					
11	TWWRUS01	29°16'31" S	26°37'51" E	1366 m	Supply water to Botshabelo Township.
12	TWWMSP02	29°01'10.3" S	26°24'9.2" E	1339 m	Supply water to the city of Bloemfontein.

Table S2. Target analytes multiple reaction monitoring transition (MRM) values.

Positive (+) Mode			Negative (-) Mode		
Q1 (m/z)	Q3 (m/z)	Analyte	Q1 (m/z)	Q3 (m/z)	Analyte
152.123	109.9	Acetaminophen 1	152.123	109.9	Acetaminophen 1
152.123	64.9	Acetaminophen 2	152.123	64.9	Acetaminophen 2
205.028	161.1	Ibuprofen 1	205.028	161.1	Ibuprofen 1
205.028	159	Ibuprofen 2	205.028	159	Ibuprofen 2
202.039	132.1	Simazine 1	202.039	132.1	Simazine 1
202.039	104.1	Simazine 2	202.039	104.1	Simazine 2
230.087	174.3	Terbutylazine 1	230.087	174.3	Terbutylazine 1
230.087	68	Terbutylazine 2	230.087	68	Terbutylazine 2
216.049	174.2	Atrazine 1	216.049	174.2	Atrazine 1
216.049	68.1	Atrazine 2	216.049	68.1	Atrazine 2
284.347	252	Metolachlor 1	284.347	252	Metolachlor 1
284.347	176.2	Metolachlor 2	284.347	176.2	Metolachlor 2
237.1	194.2	Carbamazepine 1	237.1	194.2	Carbamazepine 1
237.1	192.1	Carbamazepine 2	237.1	192.1	Carbamazepine 2
315.316	109.2	Progesterone 1	315.316	109.2	Progesterone 1
315.316	97	Progesterone 2	315.316	97	Progesterone 2
289.255	97	Testosterone 1	289.255	97	Testosterone 1
289.255	109	Testosterone 2	289.255	109	Testosterone 2
295.232	144.9	17 alpha ethynl 1	295.232	144.9	17 alpha ethyn 1
295.232	142.9	17 alpha ethynl 2	295.232	142.9	17 alpha ethyn 2
286.975	35	Triclosan 1	286.975	35	Triclosan 1
286.975	33.9	Triclosan 2	286.975	33.9	Triclosan 2
271.212	145	Estradiol 1	271.212	145	Estradiol 1
271.212	182.9	Estradiol 2	271.212	182.9	Estradiol 2

Bold numbers: The first transition values (m/z) used in this study.

Table S3. Linearity, and limit of quantification of the targeted analytes.

Analyte	Linearity (r-value)	Limit of quantification (mg/l)
Acetaminophen	0.99	0.0001
Simazine	0.99	0.01
Atrazine	0.99	0.0001
Terbutylazine	0.99	0.0001
Carbamazepine	0.99	0.01
Metolachlor	0.99	0.0001
Testosterone	0.99	0.001
Progesterone	0.99	0.001
Ibuprofen	0.99	0.1
Estradiol	0.99	0.01
Triclosan	0.99	0.1
17-alpha-ethynyl-estradiol	0.99	0.1

Table S4. Measurement of urban water quality indicators.

Urban water quality indicators	Method of analysis
EC-Electrical conductivity (µS/cm)	Hanna HI 98195 multi-parameter (onsite)
Temperature (°C)	Hanna HI 98195 multi-parameter (onsite)
DO-Dissolved Oxygen (mg/L)	Hanna HI98193 multi-parameter (onsite)
pH	Hanna HI 98195 multi-parameter (onsite)
TDS-Total Dissolved Solid (Mg/L)	Hanna HI 98195 multi-parameter (onsite)

Table S5. Descriptive statistics of water quality parameters in urban water sources and guideline values.

Water quality indicators	Summer (<i>n</i> =12)	Autumn (<i>n</i> =12)	Guideline values	
	Mean/ \pm SD	Mean/ \pm SD	SANS (2015)	WHO (2015)
Rivers (<i>n</i> =5)				
DO (mg/L)	2.55 \pm 0.39	2.94 \pm 0.64	-	-
EC (μ S/m)	351.40 \pm 118.95	479.20 \pm 136.62	170	1500
pH	7.98 \pm 0.10	8.10 \pm 0.11	5.0-9.7	6.5-8.5
TDS (mg/L)	175.60 \pm 59.65	229.20 \pm 82.56	1200	500
Temp ($^{\circ}$ C)	35.16 \pm 1.00	21.21 \pm 7.34	25	-
Dams (<i>n</i> =5)				
DO (mg/L)	2.92 \pm 0.44	3.54 \pm 1.00	-	-
EC (μ S/m)	274.20 \pm 42.24	227.20 \pm 66.41	170	1500
pH	8.03 \pm 0.23	8.08 \pm 0.26	5.0-9.7	6.5-8.5
TDS (mg/L)	137.40 \pm 21.31	114.00 \pm 33.35	1200	500
Temp ($^{\circ}$ C)	35.26 \pm 1.85	22.92 \pm 2.50	25	-
Treated drinking water (<i>n</i> =2)				
DO (mg/L)	2.37 \pm 0.35	2.49 \pm 0.27	-	-
EC (μ S/m)	95.67 \pm 152.03	207.50 \pm 30.41	170	1500
pH	4.33 \pm 4.53	8.29 \pm 0.21	5.0-9.7	6.5-8.5
TDS (mg/L)	52.20 \pm 70.85	103.00 \pm 15.56	1200	500
Temp ($^{\circ}$ C)	32.17 \pm 2.90	26.36 \pm 0.24	25	-

Notation: n=number of samples; \pm SD=standard deviation; SANS=South African National Standard; WHO=World health organisation.

Table S6. Quantification results of each selected contaminants in each sampling site.

	Sample ID	Acetaminophen (ug/L)	Simazine (mg/L)	Atrazine (mg/L)	Terbutylazine (mg/L)	Carbamazepine (ug/L)	Metolachlor (mg/L)	Testosterone (ug/L)	Progesterone (ug/L)	Ibuprofen (ug/L)	Estradiol (ug/L)	Triclosan (ug/L)	17 alpha ethyn (ug/L)
Rivers	Summer												
	SWRS03	<LOQ	0.743	0.0356	0.118	0.488	0.0716	<LOQ	<LOQ	0.753	<LOQ	<LOQ	9.2
	SWBS04	<LOQ	3.22	0.105	0.137	0.505	0.117	<LOQ	<LOQ	1.4	<LOQ	<LOQ	14.5
	SWKOR05	<LOQ	<LOQ	0.0321	0.0349	<LOQ	0.0159	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.08
	SWMO R06	<LOQ	0.119	0.0311	0.0611	0.396	0.0248	<LOQ	<LOQ	0.383	<LOQ	<LOQ	3.85
	SWKL M07	<LOQ	0.0958	0.0347	0.0477	1.43	0.0537	<LOQ	<LOQ	2.11	<LOQ	<LOQ	10.3
	Autumn												
	SWRS03	<LOQ	0.9060	0.0247	0.0309	0.3200	0.0294	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	53.8000
	SWBS04	<LOQ	0.4810	0.0184	0.0219	0.2850	0.0228	<LOQ	<LOQ	2.2600	<LOQ	<LOQ	38.0000
	SWKOR05	<LOQ	<LOQ	0.0014	0.0016	<LOQ	0.0007	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	SWMO R06	<LOQ	<LOQ	0.0099	0.0064	0.2230	0.0210	<LOQ	<LOQ	0.2220	<LOQ	<LOQ	24.6000
	SWKL M07	<LOQ	<LOQ	0.0188	0.0063	0.1680	0.0233	<LOQ	<LOQ	0.2680	<LOQ	<LOQ	9.7800
	Summer												
	SWMS01	<LOQ	0.0529	0.031	0.0416	0.0876	0.0375	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.5
Dams	SWMD02	<LOQ	0.0144	0.0308	0.0419	0.154	0.0273	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.4
	SWKDO8	<LOQ	0.235	0.0392	0.0618	0.0778	0.0392	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.99
	SWSD09	<LOQ	0.203	0.0355	0.0846	0.208	0.0238	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.01
	SWRUS D10	<LOQ	<LOQ	0.0215	0.0246	0.0107	0.0101	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.251
	Autumn												
	SWMS01	<LOQ	0.0422	0.0034	0.0070	0.0410	0.0115	<LOQ	<LOQ	0.0108	<LOQ	<LOQ	1.3000
	SWMD02	0.0936	0.0439	0.0047	0.0049	0.0335	0.0118	<LOQ	<LOQ	0.0297	<LOQ	<LOQ	4.3000
	SWKDO8	<LOQ	0.2920	0.0191	0.0296	0.0704	0.0241	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	5.8600

Treated drinking water	SWSD09	<LOQ	0.0864	0.0099	0.0068	0.0855	0.0089	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	8.2300
	SWRUSD10	<LOQ	<LOQ	0.0091	0.0026	0.1860	0.0153	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	14.8000
	Summer												
	TWWRUS01	<LOQ	<LOQ	0.0175	0.0155	<LOQ	0.00652	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.144
	TWWMSP02	<LOQ	0.039	0.119	0.161	<LOQ	0.0939	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.259
	Autumn												
	TWWRUS01	<LOQ	<LOQ	0.0083	0.0039	<LOQ	0.0038	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.4220
	TWWMSP02	<LOQ	<LOQ	0.0297	0.0172	<LOQ	0.0390	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1.0400

Table S7. Concentration of pesticides in treated drinking water with guidelines values ^{77, 79}.

Pesticides	Guideline value (mg/L)		Concentration (mg/L)	
	RSA	WHO	Summer	Autumn
Atrazine		0.01	0.07	0.02
Metolachlor		-	0.05	0.02
Simazine		0.002	<LOQ	<LOQ
Terbuthylazine		0.007	0.09	0.01

Notation: RSA=Republic of South Africa; WHO=World Health Organisation.

Table S8. The correlation coefficients among emerging contaminants in rivers.

	Acetaminophen	Simazine	Atrazine	Terbutylazine	Carbamazepine	Metolachlor	Testosterone	Progesterone	Ibuprofen	Estradiol	Triclosan	17 alpha ethinyl
Acetaminophen	1											
Simazine	0.001	1										
Atrazine	0.007	0.98	1									
Terbutylazine	0.11	0.84	0.73	1								
Carbamazepine	0.09	-0.07	-0.03	-0.06	1							
Metolachlor	0.100	0.91	0.86	0.90	0.24	1						
Testosterone	0.290	0.11	0.01	0.04	0.319	0.07	1					
Progesterone	0.087	0.20	0.23	0.40	0.234	0.347	0.43	1				
Ibuprofen	0.001	0.31	0.35	0.22	0.92	0.57	0.379	0.111	1			
Estradiol	0.192	0.01	0.31	0.33	0.48	0.34	0.001	0.518	0.198	1		
Triclosan	0.162	0.22	0.17	0.182	0.06	0.281	0.023	0.222	0.213	0.02	1	
17 alpha ethinyl	0.219	0.77	0.74	0.76	0.54	0.95	0.491	0.289	0.80	0.46	0.11	1
Acetaminophen	1											
Simazine	0.247	1										
Atrazine	0.183	0.74	1									
Terbutylazine	0.452	0.98	0.82	1								
Carbamazepine	0.0078	0.74	0.86	0.85	1							
Metolachlor	0.168	0.60	0.93	0.71	0.93	1						
Testosterone	0.222	0.40	0.21	0.234	0.319	0.347	1					
Progesterone	0.265	0.15	0.43	0.121	0.349	0.311	0.319	1				
Ibuprofen	0.200	0.23	0.24	0.35	0.39	0.20	0.0097	0.080	1			
Estradiol	0.090	0.17	0.49	0.147	0.185	0.185	0.147	0.493	0.150	1		
Triclosan	0.097	0.02	0.08	0.009	0.311	0.349	0.121	0.214	0.435	0.42	1	
17 alpha ethinyl	0.149	0.91	0.78	0.95	0.93	0.78	0.234	0.170	0.31	0.149	0.097	1

Notation: Bold number connote strong positive correlation.

Table S9. The correlation coefficients among emerging contaminants in dams during summer and autumn seasons.

	Acetaminophen	Simazine	Atrazine	Terbutylazine	Carbamazepine	Metolachlor	Testosterone	Progesterone	Ibuprofen	Estradiol	Triclosan	17 alpha ethinyl
Acetaminophen	1											
Simazine	0.307	1										
Atrazine	0.155	0.85	1									
Terbutylazine	0.145	0.86	0.81	1								
Carbamazepine	0.104	0.37	0.56	0.77	1							
Metolachlor	0.133	0.46	0.78	0.34	0.21	1						
Testosterone	0.047	0.47	0.03	0.19	0.24	0.55	1					
Progesterone	0.110	0.01	0.13	0.49	0.32	0.05	0.32	1				
Ibuprofen	0.179	0.39	0.21	0.24	0.18	0.06	0.289	0.403	1			
Estradiol	0.132	0.24	0.41	0.19	0.24	0.39	0.495	0.121	0.09	1		
Triclosan	0.203	0.33	0.30	0.03	0.37	0.27	0.153	0.258	0.34	0.22	1	
17 alpha ethinyl	0.111	0.13	0.56	0.37	0.72	0.47	0.134	0.196	0.47	0.19	0.42	1
Acetaminophen	1											
Simazine	-0.25	1										
Atrazine	-0.41	0.89	1									
Terbutylazine	-0.27	0.99	0.86	1								
Carbamazepine	-0.45	-0.23	0.22	-0.24	1							
Metolachlor	-0.24	0.81	0.83	0.86	0.14	1						
Testosterone	0.17	0.18	0.25	0.21	0.133	0.20	1					
Progesterone	0.50	0.40	0.26	0.209	0.222	0.29	0.34	1				
Ibuprofen	-0.49	0.41	0.77	0.33	0.67	0.41	0.34	0.110	1			
Estradiol	0.39	0.19	0.39	0.302	0.048	0.204	0.42	0.32	0.123	1		
Triclosan	0.233	0.14	0.07	0.05	0.034	0.106	0.135	0.09	0.40	0.48	1	
17 alpha ethinyl	-0.29	-0.20	0.27	-0.24	0.96	0.11	0.003	0.006	0.76	0.54	0.14	1

Notation: Bold number connote a strong positive correlation.

Table S10. Correlation among emerging contaminants in treated drinking water.

	Acetaminophen	Simazine	Atrazine	Terbutylazine	Carbamazepine	Metolachlor	Testosterone	Progesterone	Ibuprofen	Estradiol	Triclosan	17 alpha ethinyl
Acetaminophen	1											
Simazine	0.135	1										
Atrazine	0.48	1	1									
Terbutylazine	0.43	1	1	1								
Carbamazepine	0.42	0.15	0.19	0.306	1							
Metolachlor	0.113	1	1	1	0.085	1						
Testosterone	0.206	0.14	0.11	0.141	0.433	0.08	1					
Progesterone	0.001	0.03	0.31	0.205	0.062	0.090	0.33	1				
Ibuprofen	0.41	0.08	0.12	0.51	0.251	0.03	0.11	0.23	1			
Estradiol	0.113	0.06	0.31	0.272	0.177	0.22	0.43	0.20	0.17	1		
Triclosan	0.215	0.23	0.32	0.49	0.318	0.258	0.001	0.53	0.17	0.26	1	
17 alpha ethinyl	0.125	1	1	1	0.129	1	0.04	0.032	0.026	0.31	0.49	1
Acetaminophen	1											
Simazine	0.02	1										
Atrazine	0.21	0.33	1									
Terbutylazine	0.12	0.36	1	1								
Carbamazepine	0.52	0.12	0.50	0.30	1							
Metolachlor	0.43	0.16	1	1	0.26	1						
Testosterone	0.50	0.18	0.25	0.21	0.168	0.28	1					
Progesterone	0.14	0.16	0.16	0.42	0.196	0.034	0.111	1				
Ibuprofen	0.43	0.40	0.49	0.18	0.268	0.010	0.415	0.36	1			
Estradiol	0.13	0.08	0.09	0.035	0.121	0.023	0.37	0.18	0.12	1		
Triclosan	0.35	0.06	0.34	0.07	0.304	0.047	0.382	0.04	0.048	0.29	1	
17 alpha ethinyl	0.13	0.14	1	1	0.132	1	0.085	0.334	0.219	0.11	0.26	1

Notation: Bold number connote a strong positive correlation.

Table S11. Simplified analysis of clusters identified for emerging contaminants in water sources within Modder river catchment.

Season	Cluster group	Nodes	Contaminants per cluster	Main potential pollution source
Rivers				
Summer	C 1	1	Simazine	Wastewater effluent, agricultural runoff, and urban surface runoff.
	C 2	8	Acetaminophen, progesterone, testosterone, estradiol, metolachlor, atrazine, terbutylazine, and triclosan.	Wastewater treatment effluent, agricultural runoff, illegal dumping, and urban surface runoff.
	C 3	2	Ibuprofen, and carbamazepine.	Wastewater treatment effluent, and illegal dumping.
	C 4	1	17-alpha-ethinyl-estradiol.	Wastewater treatment effluent, and illegal dumping.
Autumn	C 1	6	Acetaminophen, metolachlor, progesterone, testosterone, atrazine, and terbutylazine.	Wastewater effluent, agricultural runoff, illegal dumping, and urban surface runoff.
	C 2	3	Estradiol, carbamazepine, and simazine.	Wastewater effluent, agricultural runoff, illegal dumping, and urban surface runoff.
	C 3	2	Triclosan, and ibuprofen	Wastewater effluent.
	C 4	1	17-alpha-ethinyl-estradiol.	Wastewater effluent, and illegal dumping.
Dams				
Summer	C 1	2	Simazine, and carbamazepine.	Wastewater effluent, illegal dumping, agricultural runoff, and domestic sewage.
	C 2	7	Acetaminophen, progesterone, testosterone, estradiol, metolachlor, atrazine, and terbutylazine.	Wastewater effluent, illegal dumping, domestic sewage, agricultural runoff, and urban surface runoff.
	C 3	2	Triclosan, and ibuprofen.	Wastewater effluent, illegal dumping, and domestic sewage.
	C 4	1	17-alpha-ethinyl-estradiol.	Wastewater effluent, illegal dumping, and domestic sewage.
Autumn	C 1	9	Acetaminophen, testosterone, progesterone, atrazine, terbutylazine, estradiol, metolachlor, ibuprofen, and carbamazepine.	Wastewater effluent, illegal dumping, domestic sewage, and agricultural runoff.
	C 2	1	Simazine.	Wastewater effluent, and agricultural runoff.
	C 3	1	Triclosan.	Wastewater effluent.
	C 4	1	17-alpha-ethinyl-estradiol.	Wastewater effluent, illegal dumping, and domestic sewage.
Treated drinking water				
Summer	C 1	6	Acetaminophen, progesterone, testosterone, estradiol, carbamazepine, and simazine.	Reservoirs used as a source of water for water treatment plants are polluted by wastewater effluent, agricultural runoff, illegal dumping, urban surface runoff and domestic sewage.
	C 2	3	Metolachlor, atrazine, and terbutylazine.	
	C 3	2	Triclosan, and ibuprofen.	
	C 4	1	17-alpha-ethinyl-estradiol.	
Autumn	C 1	7	Acetaminophen, progesterone, testosterone, simazine, estradiol, carbamazepine, and terbutylazine.	Reservoirs used as a source of water for water treatment plants are polluted by wastewater effluent, agricultural runoff, illegal dumping, urban surface runoff and domestic sewage.
	C 2	2	Atrazine, and metolachlor.	
	C 3	2	Ibuprofen, and triclosan.	
	C 4	1	17-alpha-ethinyl-estradiol	

References

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