

Supporting Information for

Mass Loading and Removal of Select Illicit Drugs in Two Wastewater Treatment Plants in New York State and Estimation of Illicit Drug Usage in Communities through Wastewater Analysis

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Table S1: Physiochemical properties of select illicit drugs and metabolites

analytes	^a Kd calculated in this study (L/kg)	^b Log Kow	^c Log Koc	^d solubility (mg/L) at 25 °C	^e stability (%)	^f excretion (%)	^f MW(par)/MW(met)
CCN	34	2.17	3.276	1298	-8.2	5	1.00
BEG	7.0	-1.32	2.548	1605	0.5	44.5	1.05
NCCN	N/A	1.96	3.173	3067	-14.4	trace	1.05
CCE	160	2.66	3.542	528.3	-9.4	0.70	0.96
APT	1245	1.76	3.045	28030	36.8	30	1
MAPT	N/A	2.22	3.207	13290	-6	43	1
MPH	88	0.72	3.473	26420	83.5	4.2	1.29
MTD	580	4.17	4.862	48.48	-10.9	27.5	1
EDDP	357	4.94	5.673	10.24	-17.1	14	1.16
MDMA	63	2.28	2.700	5413	-3.1	26	1
MDEA	N/A	2.77	2.966	1747	0.4	19	1
MDA	463	1.82	2.538	22500	-3.5	*	*

^abased on the measured concentrations of illicit drugs in influent, primary effluent, effluent, and SPM in this study; ^bbased on KOWWIN v1.67 estimate (predicted data from www.chemspider.com, based on USEPA's EPISuite™); ^cbased on PCKOCWIN v1.66; ^dbased on WSKOW V1.41; ^estability change in unfiltered raw wastewater at 2 °C after 72 h¹⁸; ^fexcretion profile of illicit drugs (unchanged and metabolite forms) and the ratio of molecular weight of parent illicit drugs and corresponding metabolite(s)³⁷; *excretion data was not available in case of MDA administered as an illicit drug despite the excretion of MDA as a metabolite of MDMA and MDEA were available.

Table S2. Characteristics of WWTPs studied

	WWTP _A	WWTP _B
primary treatment	settling	settling
secondary treatment	activated sludge	activated sludge
population served	14,675	100,000
WWTP capacity	2.5 MGD	35 MGD
average flow of wastewater	1.81 MGD (6852 m ³ /d)	22 MGD (83279 m ³ /d)
% industrial waste	~5%	~25%
hydraulic retention time	~24 h	~16 h
average sludge production	928 tons/year	5820 tons/year

Table S3. HPLC mobile phase compositions and programming for illicit drugs (Flow rate = 400 $\mu\text{L}/\text{min}$)

Time (min)	% A (methanol)	% B (0.1% formic acid in water)
0.0	5	95
2.0	10	90
2.1	30	70
4.0	30	70
6.0	50	50
7.0	50	50
7.1	65	35
10	65	35
10.1	75	25
12	75	25
12.1	90	10
13.5	90	10
14	10	90
19	10	90
20	100	0.0
25	100	0.0
26	5	95
30	5	95

Table S4. HPLC mobile phase compositions and programming for human urine indicators (Flow rate = 200 $\mu\text{L}/\text{min}$)

Time (min)	% A (methanol)	% B (0.1% formic acid in water)
0.0	30	70
0.5	30	70
1.0	20	80
2.0	20	80
12	10	90
15	10	90
16	5	95
20	5	95
25	1	99
27	95	5
32	95	5
33	30	70
38	30	70

Table S5. ESI-MS/MS parameters^a for analytes and internal standards

analytes	Q1	Q3	DP, FP, EP, CP, EXP
Cocaine (CCN)	304	182;105	30;400;6;27;7
CCN-D ₃	307	185;85	35;390;8;27;7
Benzoylcegonine (BEG)	290	168;105	35;390;9;25;7
BEG-D ₈	298	171;110	30;390;10;27;7
Norcocaine (NCCN)	290	168;136	22;390;10;22;7
NCCN-D ₃	293	171;136	28;400;10;22;7
Cocaethylene (CCE)	318	196;82	25;380;10;27;9
CCE-D ₈	326	204;85	22;390;10;27;9
Amphetamine (APT)	136	119;91	35;400;12;30;5
APT-D ₈	144	97	20;400;11;22;5
Methamphetamine (MAPT)	150	91;119	20;400;12;25;5
MAPT -D ₈	158	93;124	25;400;12;27;5
Morphine (MPH)	286	165;153	40;400;10;55;7
MPH-D ₆	292	153;165	40;400;10;55;5
Morphine-3-β-D-Glucuronide (M3G)	462	286	35;400;12;40;5
M3G-D ₃	465	289	32;400;12;42;6
Morphine-6-β-D-Glucuronide (M6G)	462	286	50;400;12;45;5
M6G-D ₃	465	289	35;400;12;45;5
Methadone (MTD)	310	265;105	10;400;10;20;12
MTD-D ₉	319	268;105	15;375;10;22;5
EDDP	278	234;249	25;400;12;38;10
EDDP-D ₃	281	234;249	30;400;12;38;10
MDA	180	105;133	15;400;12;32;5
MDA-D ₅	185	110;138	17;400;10;30;5
MDMA	194	163;105	15;375;5;15;5
MDMA-D ₅	199	165;107	20;375;12;20;6
MDEA	208	163;105	25;400;11;20;6
MDEA-D ₅	213	163;105	22;400;10;20;7
Caffeine (CFI)	195	138;110	28;400;10;25;5
CFI- ¹³ C ₃	198	140;112	25;400;9;25;5
Paraxanthine (PXT)	181	124;96	15;375;9;30;5
PXT-D ₆	187	127;91	20;375;9;30;5
Nicotine (NCT)	163	117;130	40;300;6;40;5
NCT-D ₃	166	117;130	40;300;6;40;5
Cotinine (CTN)	177	80;98	27;350;12;35;5
CTN-D ₃	180	80;101	27;350;12;35;5

DP: declustering potential; FP: focusing potential; EP: entrance potential; CP: collision potential; EXP: exit potential

^asource parameters: ion spray voltage (4500 V) and temperature (450 °C)

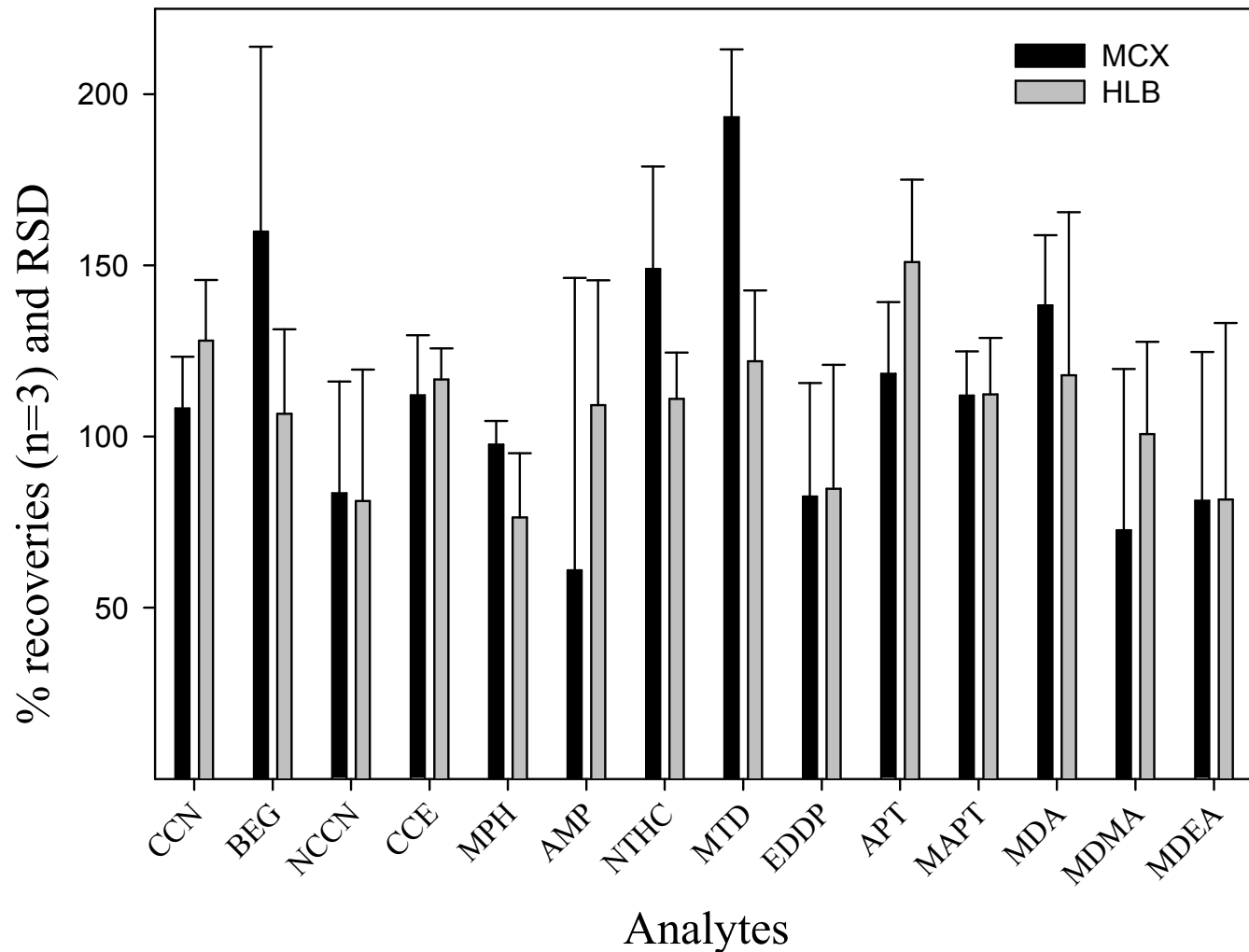
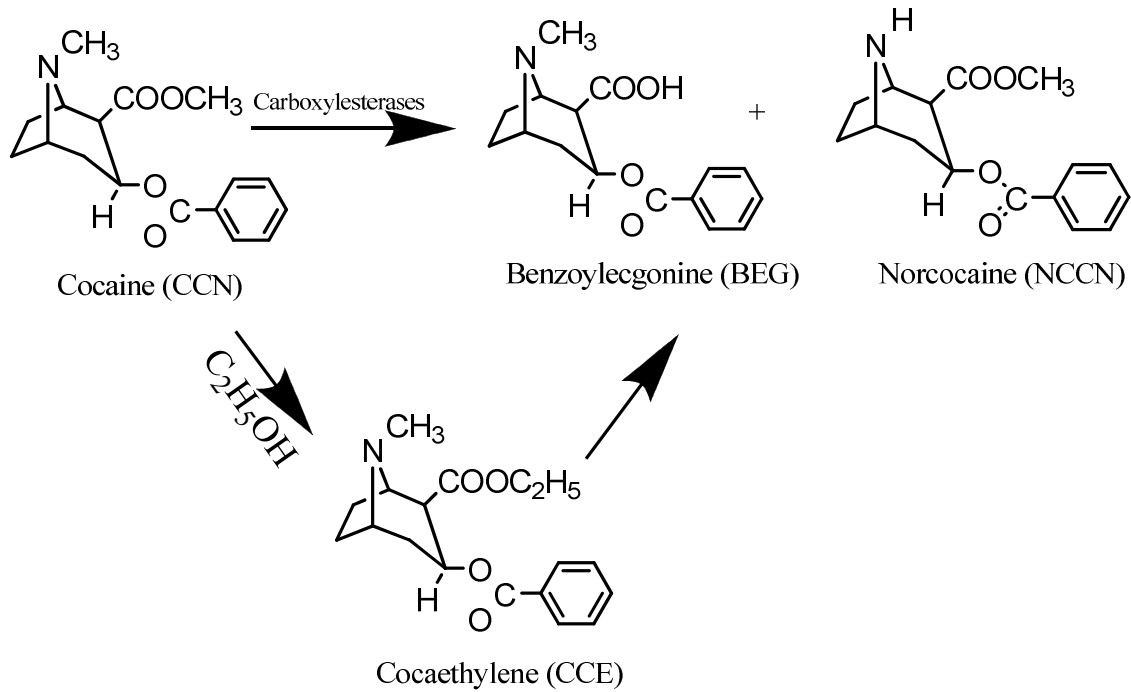


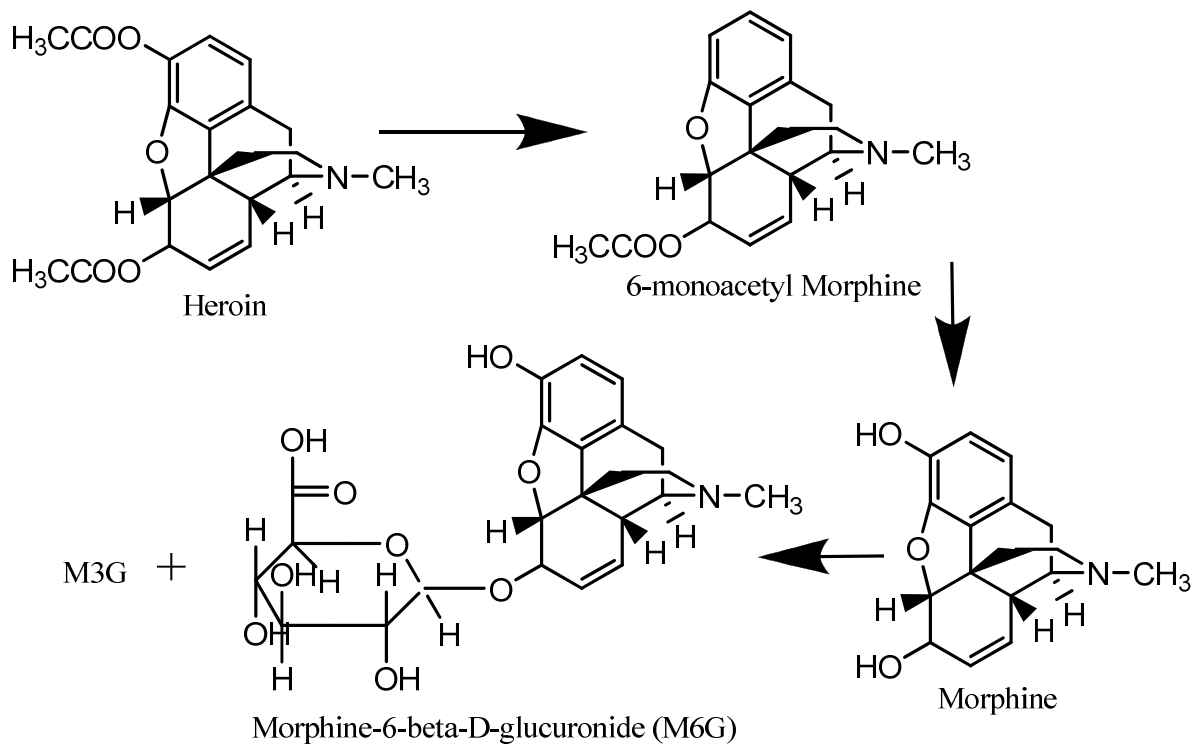
Figure S1: Spiking recoveries and relative standard deviations (n=3) of illicit drugs through MCX and HLB cartridges.

Frequency and Doses of Use of Illicit Drugs: The frequency and doses of illicit drugs ingested by the population were calculated based on mass loadings of illicit drugs to the WWTPs and the amount of the drugs ingested for every dose.³⁷ The estimated number of doses of CCN per day in the communities served by WWTP_A and WWTP_B were 165 and 3509, respectively (Table 2). The total number of doses corresponds 1.68 and 5.26% of the population of age 15-64, which is ~4.2-18 times higher than the UNODC's estimation of global CCN consumption (0.3-0.4% of global adult population of age 15-64 in 2011). Similarly, 0.52 and 0.93% of the population served by WWTP_A and WWTP_B were found to abuse APT, which was similar to the UNDOC's estimation of 0.7%.² The total doses of MPH were found to be 3151 and 29810 in the communities served by WWTP_A and WWTP_B, corresponding to 32 and 45% of the population; however, the existence of multiple sources of MPH (as discussed above) suggested that this estimate does not only represent illegal usage but also legal usage.

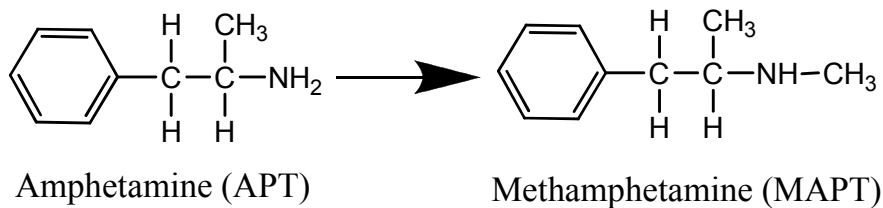
Metabolization of cocaine (MPH)



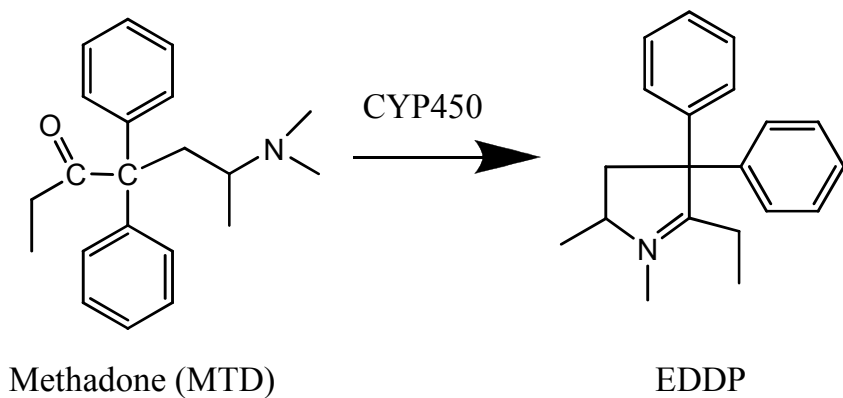
Metabolization of heroine



Metabolization of amphetamine (APT)



Metabolization of methadone (MTD)



Metabolization of MDMA and MDEA

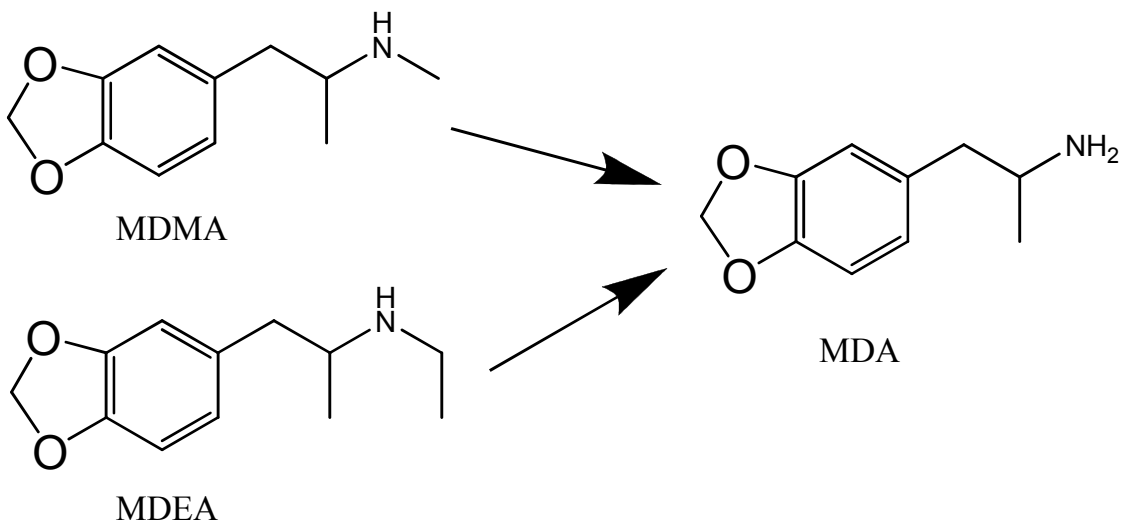


Figure S2: Metabolization of select illicit drugs in human

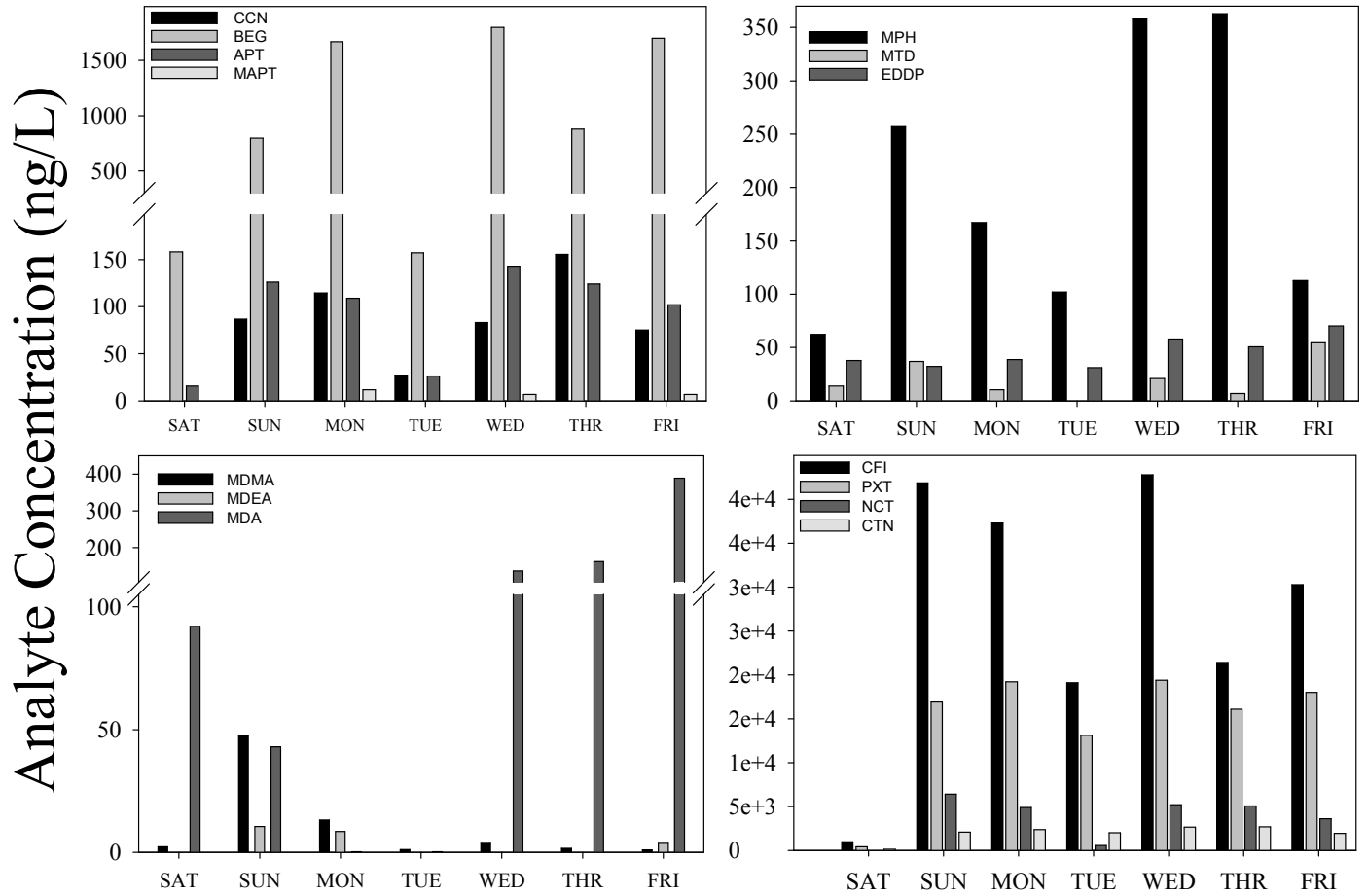


Figure S3: Daily trends of illicit drugs and bioindicators in WWTP_A.

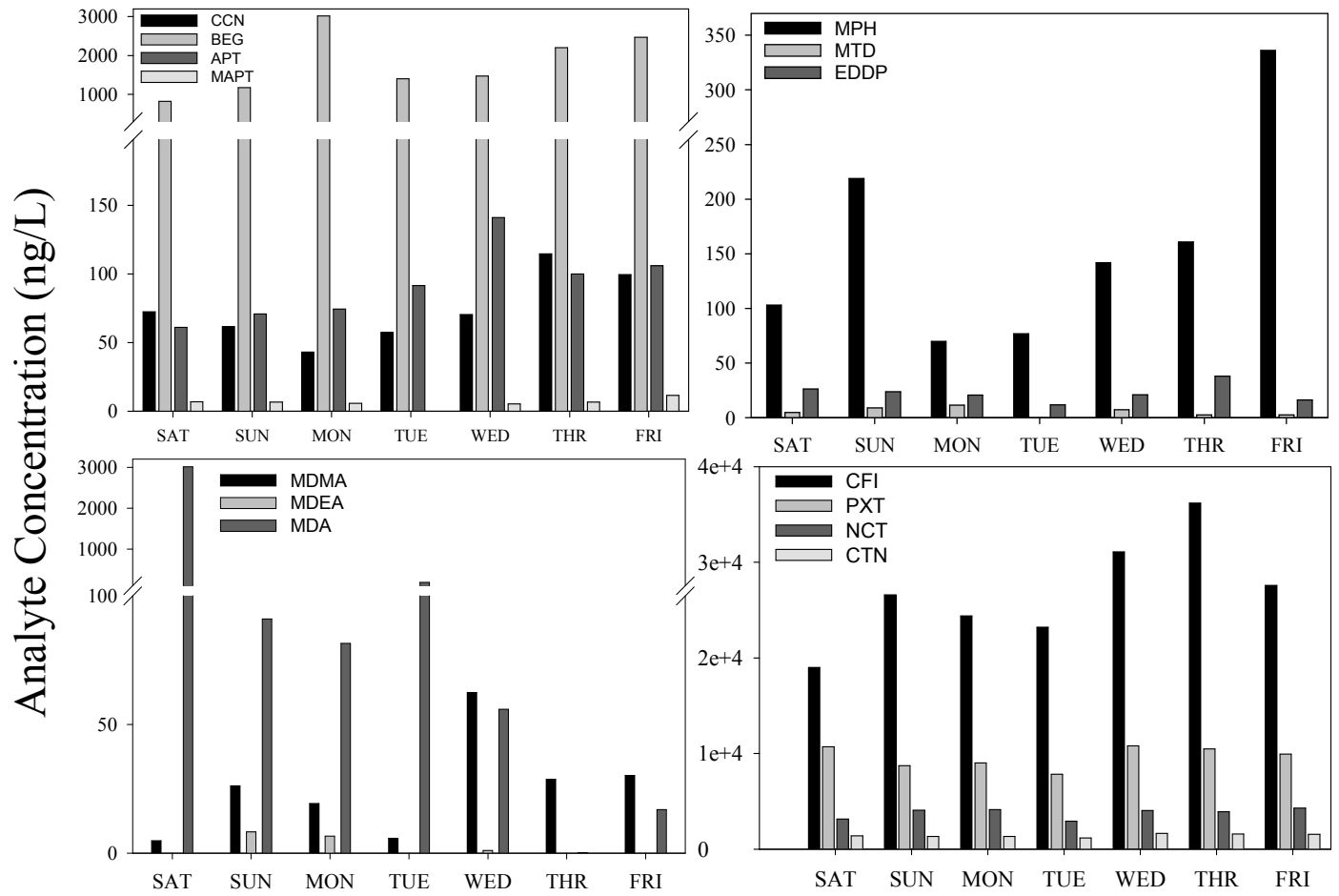


Figure S4: Daily trends of illicit drugs and bioindicators in WWTP_B.