Supporting Information

Occurrence of Natural and Synthetic Glucocorticoids in Sewage Treatment Plants and Receiving River Waters

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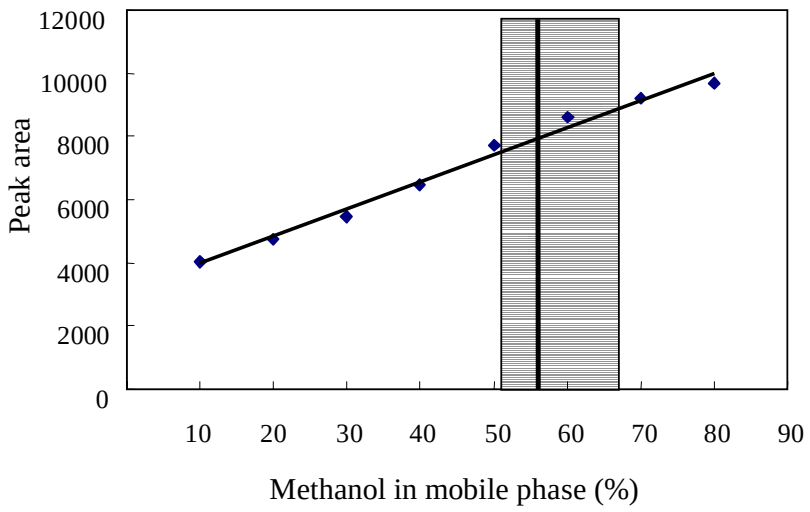

FIGURE S1 Response of cortisol-d_2 at different methanol proportion in mobile phase. The gray part refers to the proportion of methanol eluting target analytes in gradient elution of this study.

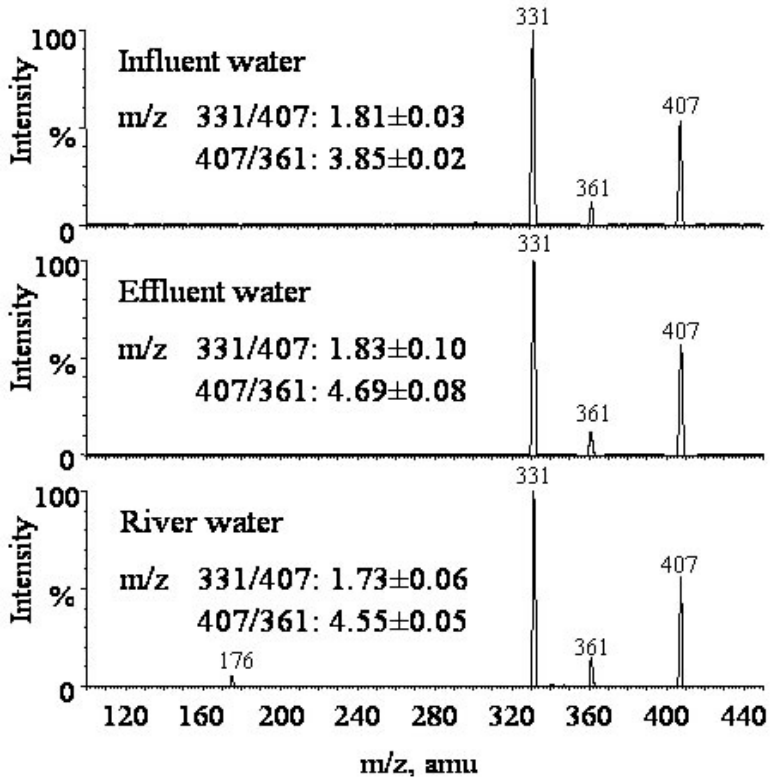

FIGURE S2 (a) MS-spectra and ion ratios (by abundance) for spiked cortisol in different water matrices.

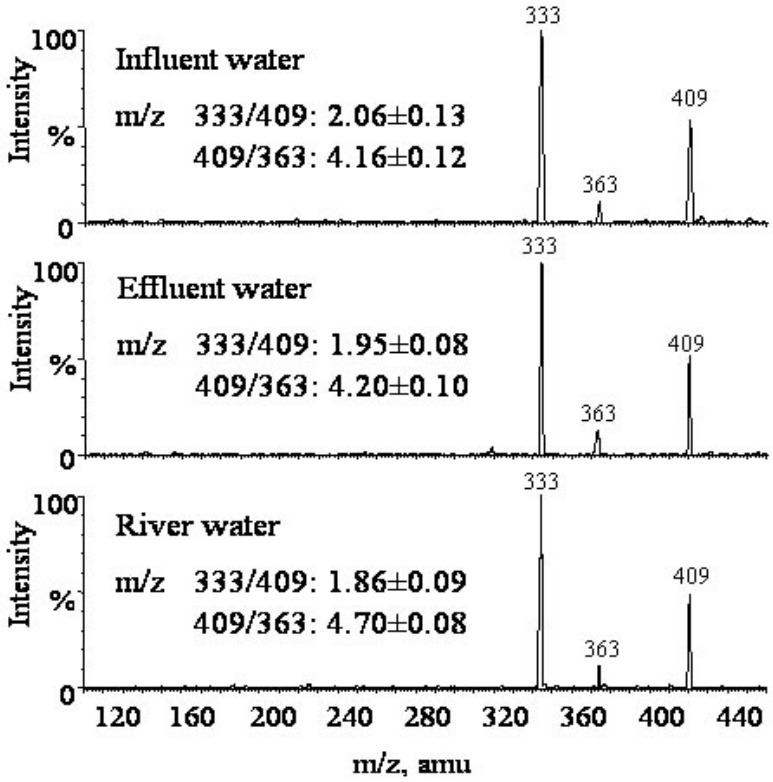

FIGURE S2 (b) MS-spectra and ion ratios (by abundance) for spiked cortisol-d_2 in different water matrices.

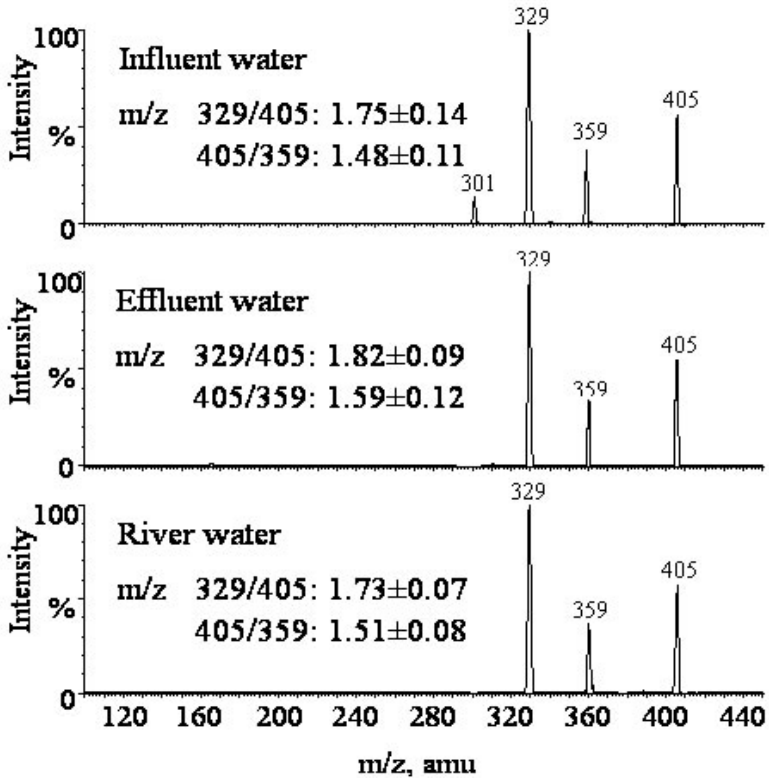

FIGURE S2 (c) MS-spectra and ion ratios (by abundance) for spiked cortisone in different water matrices.

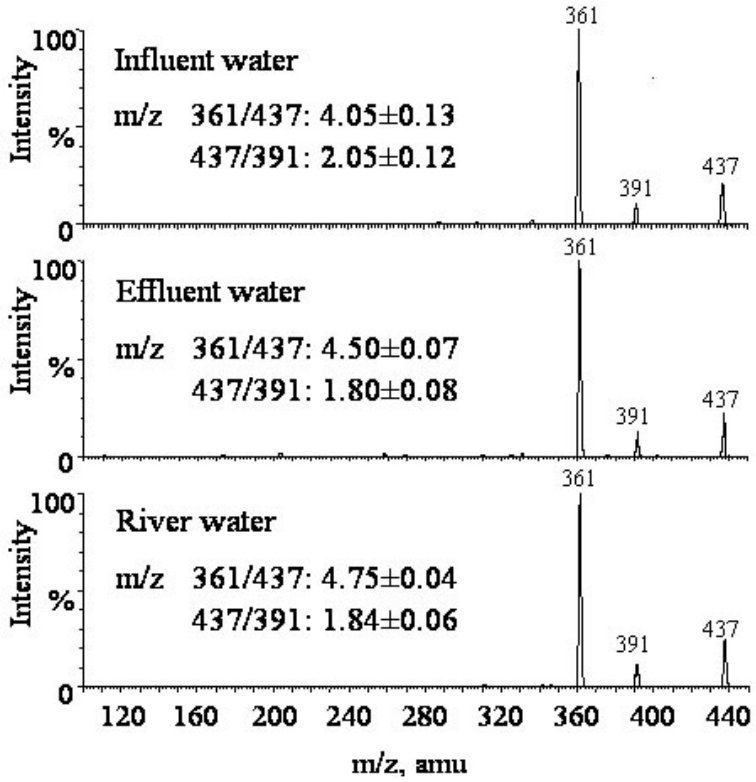

FIGURE S2 (d) MS-spectra and ion ratios (by abundance) for spiked dexamethasone in different water matrices.

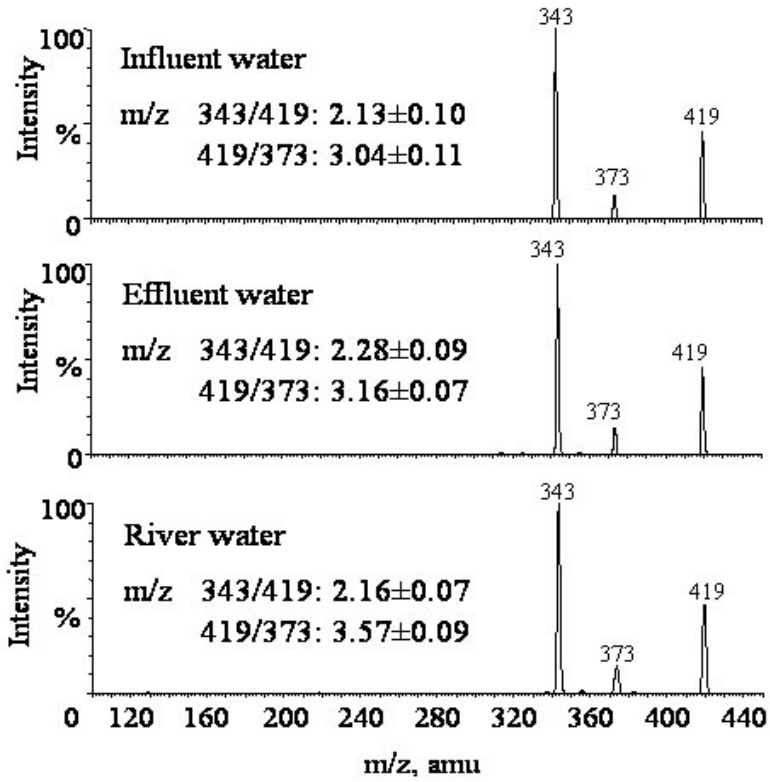

FIGURE S2 (e) MS-spectra and ion ratios (by abundance) for spiked 6α-mpp in different water matrices.

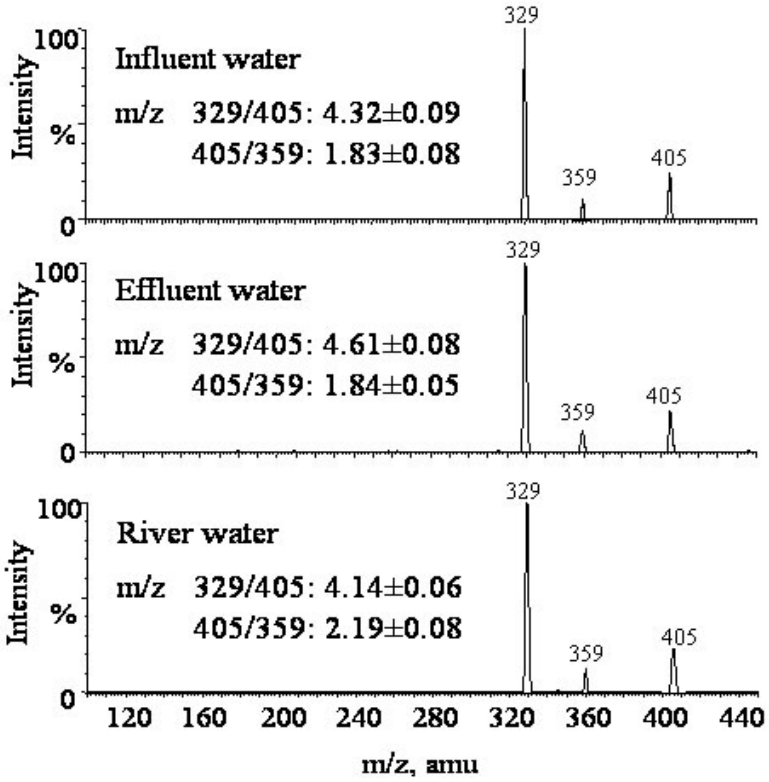

FIGURE S2 (f) MS-spectra and ion ratios (by abundance) for spiked prednisolone in different water matrices.

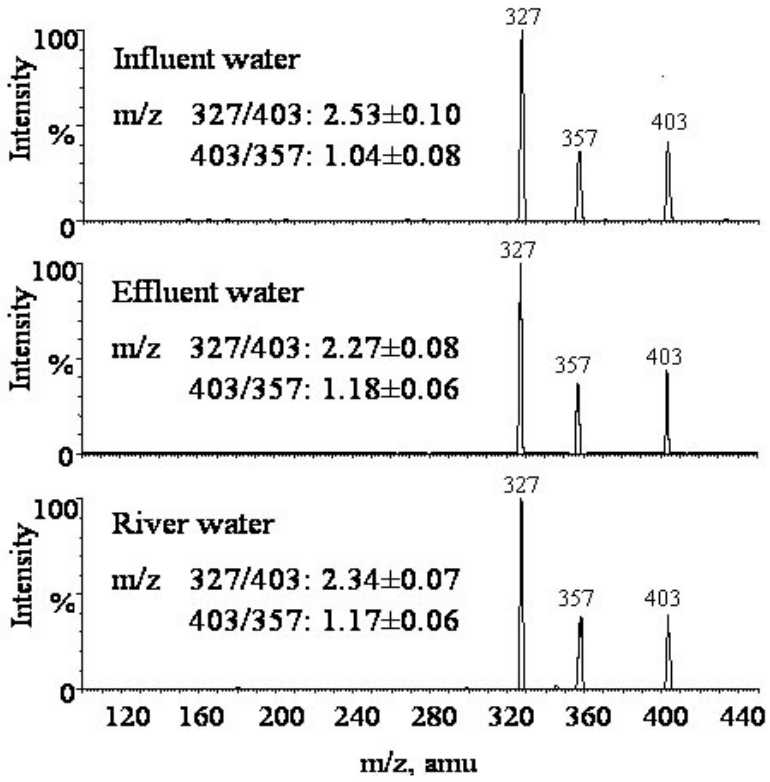

FIGURE S2 (g) MS-spectra and ion ratios (by abundance) for spiked prednisone in different water matrices.

Table S1. Some Available Technical Characteristics of the Six Activated Sludge Sewage Treatment Plants (STP) Considered in This Study*

STP	Inhabitants	Loading m^3/day	HRT,[a] h	SRT,[b] d	TSS,[c,f] in/out mg/L	BOD_5,[d,f] in/out mg/L	COD_{cr},[e,f] in/out mg/L
Beixiaohe	400 000	60 000	6-7	5.2	199/12	165/9	341/40
Fangzhuang	100 000	40 000	9.7	10	344/11	295/9	612/38
Gaobeidian	2400 000	791 500	9	10-12	278/10	159/8	329/34
Jiuxianqiao	480 000	200 000	8-11	10.2-18	170/11	154/9	318/38
Qinghe	814 000	474 300	13.5	12.2-17	299/11	194/9	404/40
Wujiacun	180 000	15 000	7	11	116/11	104/9	211/39
Xiaohongmen	1925 000	600 000	12.5	12	355/13	221/10	454/44

*all STPs contained anaerobic, anoxic and aerobic process excepte Beixiaohe STP, which only contained the latter two processes. [a]HRT = hydraulic residence time; [b]SRT = solid residence time; [c]TSS = total suspended solids; [d]BOD_5 = five-day biochemical oxygen demand; [e]COD_{cr} = chemical oxygen demand consumption using the dichromate method. [f] averaged values during this study.

Table S2 Recoveries of the Six Glucocorticoids spiked into seven STP influents [a]

compound	Recovery, [b] % ± RSD						
	Cortisol	Cortisol-d_2	Cortisone	Dexamethasone	6α-Methylprednisolone	Prednisolone	Prednisone
Beixiaohe	92 ± 3.5	82 ± 4.6	87 ± 5.2	86 ± 4.9	80 ± 2.9	82 ± 4.2	87 ± 9.4
Gaobeidian	87 ± 4.2	85 ± 6.6	81 ± 15	81 ± 7.6	73 ± 2.1	79 ± 1.7	99 ± 4.4
Fangzhuang	84 ± 7.8	87 ±13	83 ± 4.2	87 ± 8.7	81 ± 3.8	83 ± 4.7	95 ± 5.8
Jiuxianqiao	79 ± 9.2	89 ± 5.6	88 ± 10	84 ± 7.3	83 ± 12	85 ± 13	97 ± 4.1
Qinghe	86 ± 6.7	81 ± 5.0	82 ± 3.9	85 ± 9.4	79 ± 4.6	86 ± 9.4	93 ± 7.8
Wujiacun	91 ± 4.1	92 ± 4.9	84 ± 5.3	82 ± 13	81 ± 8.2	84 ± 6.1	98 ± 10
Xiaohongmen	87 ± 5.2	85 ± 9.1	79 ± 11	86 ± 9.8	78 ± 6.7	80 ± 7.4	89 ± 11

[a] Spiked concentration in the range of 20-120 ng/L. [b] Mean values from three determinations by external standard quantification procedures.

Table S3 Concentrations and Percent Removals of Glucocorticoids in the Biological Treatment of Gaobeidian STP

Analyte	Concentration, ng/L				Percent removal, %		
	Primary effluent	Anaerobic effluent	Anoxic effluent	Aerobic effluent	Anaerobic treatment	Anoxic effluent	Aerobic effluent
Cortisol	65	5.6	0.43	0.28	91	92	36
Cortisone	83	8.0	0.07	0.06	90	99	6
Dexamethasone	3.4	0.43	0.03	<0.1	87	94	-
6α-Methylprednisolone	2.3	0.26	<0.08	<0.08	89	-	-
Prednisolone	5.0	1.4	0.91	0.89	72	35	2
Prednisone	4.5	0.29	<0.1	<0.1	94	-	-

LOQ is 0.2 ng/L for cortisone, 0.08 ng/L for 6α-methylprednisolone and 0.1 ng/L for the other four glucocorticoids in the four type of effluents.

Table S4 Concentrations (ng/L) of Six Glucocorticoids in Tonghui River in June and July 2006[a]

Location	Date	Cortisol	Cortisone	Dexmethasone	6α-Methylprednisolone	Prednisolone	Prednisone	Ratio[b]
upstream 2 km		0.46	0.27	0.06	0.07	0.30	<0.01	2
gaobeidian STP effluent		0.43	0.26	<0.01	<0.01	0.64	<0.01	1
downstream 0.5 km	2006/7/2	0.43	0.23	0.05	0.06	0.28	<0.01	2
downstream 0.55 km		1.0	1.1	0.07	0.04	0.27	<0.01	8
downstream 2.55 km		<0.01	0.06	0.05	0.05	0.05	<0.01	1
upstream 2 km		0.54	0.58	0.06	<0.01	0.27	<0.01	4
gaobeidian STP effluent		0.43	0.44	<0.01	<0.01	0.56	<0.01	2
downstream 0.5 km	2006/7/9	0.51	0.43	0.06	<0.01	0.28	<0.01	3
downstream 0.55 km		1.2	2.1	0.13	<0.01	0.30	0.12	11
downstream 2.55 km		1.7	2.6	0.17	0.08	0.11	0.15	39
upstream 2 km		0.26	0.25	0.04	0.07	0.31	<0.01	2
gaobeidian STP effluent		0.32	0.28	<0.01	<0.01	0.48	<0.01	1
downstream 0.5 km	2006/7/16	0.24	0.26	0.03	0.05	0.32	<0.01	2
downstream 0.55 km		0.42	0.63	0.04	0.05	0.31	<0.01	3
downstream 2.55 km		0.16	<0.02	0.03	0.06	<0.01	<0.01	-
upstream 2 km		0.24	0.16	0.02	<0.01	0.25	<0.01	2
gaobeidian STP effluent		0.28	0.20	<0.01	<0.01	0.60	<0.01	1
downstream 0.5 km	2006/7/23	0.18	0.19	0.03	<0.01	0.32	<0.01	1
downstream 0.55 km		3.4	4.2	0.31	<0.01	0.24	0.86	32
downstream 2.55 km		0.16	<0.02	0.03	<0.01	0.03	<0.01	5

[a]Average of duplicate injections. LOQ is 0.02 ng/L for cortisone and 0.01 ng/L for other five glucocoticoids in river water. [b]Between the combined concentrations of two natural glucocorticoids (cotisol and cotisone) and the concentration of one synthetic glucocorticoid, prednisolone.

Table S5 Concentrations (ng/L) of Six Glucocorticoids in Qing River in June and July 2006[a]

Location	Date	Cortisol	Cortisone	Dexmethasone	6α-Methylprednisolone	Prednisolone	Prednisone	Ratio[b]
upstream 4 km		<0.01	<0.02	0.04	<0.01	0.32	<0.01	-
upstream 2 km		0.30	0.23	0.10	<0.01	0.28	<0.01	2
qinghe STP effluent	2006/7/2	0.56	0.30	<0.01	<0.01	0.58	<0.01	2
downstream 2 km		2.6	1.5	0.11	<0.01	0.36	<0.01	11
downstream 4 km		2.1	1.7	0.08	<0.01	0.29	<0.01	13
upstream 4 km		0.24	0.18	0.04	<0.01	0.31	<0.01	1
upstream 2 km		0.40	0.42	0.04	<0.01	0.27	<0.01	3
qinghe STP effluent	2006/7/9	0.58	0.17	<0.01	<0.01	0.50	<0.01	2
downstream 2 km		0.79	0.53	0.02	<0.01	0.31	<0.01	4
downstream 4 km		0.77	0.40	0.02	<0.01	0.27	<0.01	4
upstream 4 km		0.10	0.14	0.03	<0.01	0.31	<0.01	1
upstream 2 km		0.13	0.19	0.05	<0.01	0.27	<0.01	1
qinghe STP effluent	2006/7/16	0.38	0.17	0.03	<0.01	0.75	<0.01	1
downstream 2 km		0.68	0.32	<0.01	<0.01	0.33	<0.01	3
downstream 4 km		0.74	0.32	0.04	<0.01	0.32	<0.01	3
upstream 4 km		0.08	<0.02	0.02	<0.01	0.30	<0.01	-
upstream 2 km		0.27	0.28	0.02	<0.01	0.23	<0.01	2
qinghe STP effluent	2006/7/23	0.61	0.19	<0.01	<0.01	0.54	<0.01	1
downstream 2 km		0.92	0.34	<0.01	<0.01	0.29	<0.01	4
downstream 4 km		0.31	0.08	0.02	<0.01	0.11	<0.01	3

[a]Average of duplicate injections. LOQ is 0.02 ng/L for cortisone and 0.01 ng/L for other five glucocoticoids in river water. [b]Between the combined concentrations of two natural glucocorticoids (cotisol and cotisone) and the concentration of one synthetic glucocorticoid, prednisolone.