Supplementary Information

Metabolomics-based Screening Analysis on PPCPs in Water Pretreated with Five Different SPE Columns†

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7 Pages, 3 Tables, 5 Figures

Table S1 Average recovery and RSD (%) for 50 μg·L^{-1} PPCPs in pure water (*n*=9)

Table S1 Average recovery and RSD (%) for 50 μg·L^{-1} PPCPs in pure water (n=9)

No.	Compounds	Cleanert PEP-2 (60 mg/3 mL)	Oasis HLB (60 mg/3 mL)	ProElut PLS (60 mg/1 mL)	ProElut PLS (60 mg/3 mL)	ProElut PLS (100 mg/6 mL)
1	Clorprenaline	**47**/3.0	24/4.3	39/2.9	33/3.4	22/6.1
2	Ractopamine	**49**/3.2	28/4.4	32/3.3	37/4.0	23/6.0
3	Orbifloxacin	**47**/3.7	23/4.7	31/3.4	38/4.8	41/4.9
4	Betaxolol	**43**/2.9	27/3.5	28/4.5	21/6.1	30/3.2
5	Brombuterol	**44**/3.4	36/2.9	32/3.2	19/5.8	29/4.3
6	Cimaterol	**49**/3.0	22/5.4	40/2.7	28/3.5	31/3.4
7	Cefotaxime	**41**/3.2	20/5.1	33/3.4	29/4.5	29/5.1
8	Josamycin	**44**/3.1	19/4.7	30/5.1	32/4.4	36/4.8
9	Glibenclamide	**47**/3.7	36/3.2	35/4.2	29/3.7	21/5.7
10	Difloxacin	**55**/3.2	32/4.0	22/4.1	47/4.2	21/5.4
1	Albendazole	44/3.7	**51**/2.9	25/4.4	40/3.7	22/5.5
2	Sulfmethazine	22/5.2	**54**/3.1	34/5.2	34/4.4	35/4.2
3	Sparfloxacin	35/4.4	**44**/3.3	27/5.3	33/4.2	21/6.1
4	Lomefloxacin	36/3.9	**44**/3.7	35/4.8	21/5.4	27/5.8
5	Fleroxacin	33/2.9	**48**/2.9	31/4.4	22/5.0	28/4.7
6	Enrofloxacin	27/3.1	**41**/4.4	24/5.8	22/5.5	20/5.9
7	Pipemidic acid	33/4.2	**47**/3.8	29/4.4	23/4.8	25/5.0
8	Ciprofloxacin	33/4.8	**42**/4.8	30/3.2	26/4.1	19/5.5
9	Norfloxacin	24/5.0	**43**/5.2	27/4.4	30/3.3	21/4.7
10	Ofloxacin	37/3.3	**45**/3.0	27/5.8	22/5.5	31/4.3
11	Enoxacin	33/3.9	**41**/4.1	27/4.2	29/4.3	20/5.9
12	Sulfamethizole	27/4.8	**38**/4.2	22/5.6	23/4.0	18/6.2
13	Hydrocortisone 17-valerate	20/4.9	**42**/3.9	23/4.4	24/5.3	21/5.4
14	Marbofloxacin	33/3.7	**44**/4.6	28/4.9	21/5.0	26/4.4
15	Sulfathiazole	23/5.1	**49**/4.7	40/3.4	34/4.7	38/3.9
1	Nalidixic acid	34/2.8	31/4.0	**47**/3.6	38/3.3	20/5.4
2	Trimethoprim	38/4.9	22/5.9	**45**/4.2	32/4.2	38/4.4
3	Sulfamerazine	38/4.1	22/6.2	**47**/3.1	33/4.4	31/4.5
4	Atenolol	27/5.7	21/5.3	**44**/5.2	35/3.8	35/3.9
5	Lincomycin	30/4.4	23/4.9	**48**/3.3	39/4.3	40/4.2
6	Sulfadiazine	21/5.9	35/4.6	**46**/4.0	37/4.2	34/5.4
7	Indoprofen	20/6.2	31/3.9	**42**/4.0	24/5.6	31/4.7
8	Nadolol	32/3.3	23/4.8	**48**/3.2	39/5.1	39/3.2
9	Tenoxicam	35/4.5	25/4.7	**51**/3.7	37/3.9	40/3.2
10	Ronidazole	24/5.1	34/3.4	**49**/3.3	37/3.3	37/4.1
11	Piroxicam	32/4.8	21/5.6	**47**/4.1	38/4.2	38/3.8
12	Cefaclor	24/5.5	21/5.0	**43**/3.8	27/4.8	29/4.0
13	Flumequine	41/3.8	25/4.8	**52**/4.0	43/3.4	41/3.7
14	Cephalexin	27/4.4	22/6.2	**46**/4.1	28/4.7	30/3.6
15	Sulfachloropyridazine	35/4.2	22/5.8	**49**/3.2	37/3.3	37/3.0
16	Triamcinolone diacetate	27/5.4	22/5.5	**45**/2.9	34/4.2	34/4.2
17	Danofloxacin	22/5.1	24/4.8	**49**/4.7	33/3.4	29/5.0
18	Cefapirin	32/3.8	24/5.5	**52**/4.1	40/4.0	42/3.4
19	Cortisone	40/3.5	21/5.8	**50**/4.4	42/4.1	42/3.4
20	Metronidazole	28/4.1	38/4.2	**51**/3.8	37/3.8	22/5.9
21	Triamcinolone acetonide 21-acetate	21/5.5	25/4.8	**44**/4.2	30/4.3	29/4.8
22	Ipronidazole	28/4.6	19/5.7	**40**/4.2	33/4.3	32/3.4
23	Cinoxacin	28/5.1	33/3.9	**58**/3.4	37/4.4	45/4.3
24	Cefadroxil	24/5.0	19/4.9	**39**/4.1	29/5.2	30/4.7
25	Cefixime	20/5.6	22/5.7	**44**/2.8	31/5.0	34/4.5
26	Ceftiofur	21/5.7	24/4.9	**44**/4.4	29/5.9	25/5.4
27	Sulindac	22/4.9	28/3.6	**49**/3.9	31/4.8	30/4.3
28	Sasapyrine	27/3.0	21/5.5	**43**/3.2	34/4.5	28/3.9
1	Repaglinde	22/5.8	23/4.4	36/4.5	**46**/4.4	28/4.3
2	Cefetamet pivoxyl	21/5.7	27/5.2	29/5.1	**44**/5.1	24/3.9
3	Sulfaquinoxaline	22/5.5	24/4.4	21/5.5	**44**/3.9	27/4.5
4	Sulfabenzamide	20/6.1	18/5.8	33/4.7	**40**/4.1	24/5.2
5	Sulfanitran	27/4.5	34/4.2	21/5.6	**43**/4.3	28/3.3
1	Dimetridazole	33/3.9	32/3.3	20/6.2	22/6.1	**41**/3.9
2	Beclomethasone	21/5.5	33/4.7	27/4.4	30/5.1	**44**/3.7
3	Sulfamoxole	21/5.1	32/3.8	26/4.2	33/3.3	**43**/3.3
4	Betamethasone dipropionate	22/5.2	30/4.4	36/4.8	40/4.0	**49**/3.7
5	Hydrocortisone	27/4.4	21/5.2	23/5.4	29/4.8	**44**/3.5

Table S1 Average recovery and RSD (%) for 50 μg·L^{-1} PPCPs in pure water (*n*=9)

6	Cephradine	21/5.4	27/4.8	24/5.6	21/5.5	**54**/3.2

Note: bold numbers represent the highest recoveries among five SPE column groups.

Table S2 Average recovery and RSD (%) for 1 μg·L^{-1} PPCPs in reservoir water (*n*=9)

No.	Compounds	Cleanert PEP-2 (60 mg/3 mL)	Oasis HLB (60 mg/3 mL)	ProElut PLS (60 mg/1 mL)	ProElut PLS (60 mg/3 mL)	ProElut PLS (100 mg/6 mL)
1	Clorprenaline	**49**/3.8	24/4.4	36/4.2	34/3.8	27/4.4
2	Ractopamine	**50**/3.3	24/5.6	33/3.6	40/3.2	24/4.2
3	Orbifloxacin	**49**/3.5	22/5.0	29/5.1	39/4.1	41/3.7
4	Betaxolol	**45**/3.1	28/4.2	27/4.2	22/5.7	32/3.5
5	Cimaterol	**47**/4.4	22/4.7	41/3.7	26/3.4	33/4.1
6	Brombuterol	**45**/4.2	32/4.4	30/4.4	21/5.8	30/3.7
7	Josamycin	**46**/3.6	21/5.6	29/3.2	33/4.1	37/3.2
8	Cefotaxime	**44**/3.2	21/5.6	35/4.3	26/3.2	27/4.3
9	Glibenclamide	**49**/4.1	34/4.2	34/4.1	29/5.6	23/4.5
10	Difloxacin	**52**/3.9	33/4.3	24/5.0	45/4.1	23/4.8
1	Albendazole	40/4.2	**52**/3.2	27/4.3	42/3.4	24/4.9
2	Sulfmethazine	25/5.4	**54**/3.0	37/4.0	36/3.5	35/3.2
3	Sparfloxacin	33/4.5	**43**/3.8	29/4.1	34/4.0	21/5.6
4	Fleroxacin	31/4.3	**47**/4.8	33/3.5	21/5.8	27/4.8
5	Lomefloxacin	38/3.8	**45**/4.0	33/4.2	22/5.6	25/4.6
6	Enrofloxacin	29/5.0	**44**/4.1	23/5.6	25/4.3	21/5.0
7	Ciprofloxacin	31/4.7	**44**/4.4	29/4.8	24/4.3	20/6.1
8	Pipemidic acid	29/5.5	**46**/3.2	28/4.4	22/5.4	23/3.9
9	Norfloxacin	22/5.4	**41**/3.3	26/4.3	28/4.2	20/5.8
10	Ofloxacin	35/4.0	**46**/3.9	29/4.5	22/4.8	29/4.4
11	Enoxacin	35/3.4	**44**/3.8	25/3.9	25/3.9	21/5.6
12	Sulfamethizole	31/4.8	**46**/3.4	22/5.2	25/4.7	22/5.7
13	Hydrocortisone 17-valerate	22/5.2	**43**/4.1	27/4.7	26/4.3	21/5.9
14	Marbofloxacin	31/3.8	**46**/3.5	26/4.3	23/5.6	22/4.4
15	Sulfathiazole	25/4.5	**51**/3.7	44/4.0	31/4.1	38/3.2
1	Nalidixic acid	32/4.3	33/4.2	**46**/3.2	34/4.4	22/5.1
2	Trimethoprim	35/3.3	21/5.5	**47**/3.0	33/4.2	38/4.3
3	Sulfamerazine	36/3.9	22/5.0	**45**/3.1	30/3.9	33/3.4
4	Atenolol	24/4.8	22/5.1	**46**/3.4	32/2.8	34/3.4
5	Lincomycin	28/4.8	24/4.8	**51**/2.9	40/3.1	39/3.2
6	Indoprofen	22/5.7	33/4.4	**47**/3.4	26/4.6	33/4.0
7	Sulfadiazine	22/5.5	37/4.5	**45**/3.2	33/3.9	33/3.4
8	Nadolol	30/3.4	22/5.1	**48**/2.9	35/3.5	37/3.2
9	Tenoxicam	37/4.0	24/4.3	**49**/4.0	36/3.5	41/3.9
10	Ronidazole	25/5.1	33/4.1	**51**/3.1	34/3.1	32/4.0
11	Piroxicam	30/4.4	22/5.6	**45**/3.4	36/4.0	36/4.0
12	Flumequine	38/4.2	23/5.1	**51**/3.0	44/4.0	44/3.2
13	Cefaclor	23/5.0	21/4.8	**44**/4.0	28/3.4	28/3.8
14	Cephalexin	25/4.5	24/4.4	**51**/3.8	28/4.1	32/4.0
15	Sulfachloropyridazine	33/4.3	24/4.0	**49**/3.2	33/3.7	33/3.4
16	Triamcinolone diacetate	27/4.1	21/5.1	**44**/3.3	32/3.3	33/4.1
17	Danofloxacin	23/5.1	24/4.7	**47**/4.1	30/3.4	31/3.5
18	Cortisone	40/4.2	22/4.7	**50**/3.2	41/3.2	43/3.1
19	Cefapirin	30/4.5	25/4.0	**51**/3.4	42/4.0	42/3.7
20	Metronidazole	24/5.0	35/4.1	**51**/2.9	33/3.9	25/4.6
21	Triamcinolone acetonide 21-acetate	23/4.9	22/5.6	**46**/3.5	32/3.5	31/5.0
22	Ipronidazole	27/3.4	22/5.4	**46**/3.4	37/3.2	32/3.4
23	Cinoxacin	24/3.6	32/4.7	**56**/3.1	35/3.4	44/4.0
24	Cefadroxil	20/4.8	22/5.4	**44**/4.0	26/5.1	28/3.4
25	Cefixime	21/4.9	23/5.0	**43**/3.2	30/3.4	33/4.1
26	Ceftiofur	22/4.4	22/6.1	**47**/3.3	26/4.8	25/4.8
27	Sulindac	22/4.9	23/4.3	**45**/3.0	34/3.7	35/3.2
28	Sasapyrine	27/3.4	22/5.4	**46**/3.2	37/3.5	29/4.1
1	Repaglinde	25/4.1	22/5.5	34/4.1	**45**/3.2	25/4.0
2	Cefetamet pivoxyl	22/4.2	24/4.7	30/3.4	**47**/2.9	23/4.5
3	Sulfaquinoxaline	21/4.3	25/4.3	21/5.6	**43**/3.2	25/4.5
4	Sulfabenzamide	20/5.1	22/4.8	31/2.9	**42**/4.4	27/3.4
5	Sulfanitran	24/4.7	33/4.3	20/4.8	**42**/4.5	29/4.2

Table S2 Average recovery and RSD (%) for 1 μg·L^{-1} PPCPs in reservoir water (n=9)

1	Dimetridazole	34/4.1	34/4.4	21/5.6	23/5.7	**43**/3.3
2	Beclomethasone	22/4.6	32/4.5	28/4.0	28/3.2	**45**/3.2
3	Sulfamoxole	24/3.4	33/3.8	23/4.8	36/3.8	**48**/3.1
4	Betamethasone dipropionate	21/5.0	32/4.2	36/3.4	38/3.1	**46**/3.2
5	Hydrocortisone	26/4.3	22/5.1	25/4.3	27/4.2	**45**/3.0
6	Cephradine	21/4.6	26/4.8	24/3.4	26/3.9	**49**/3.2

Note: bold numbers represent the highest recoveries among five SPE column groups.

Table S3 'Biomarkers' screened in positive ion mode (1 μg·L^{-1} PPCPs in reservoir water)

SPE column	No.	Var ID (Primary)	Biomarker	VIP pred	Coordinate in S-plot	Mass error (ppm)
Cleanert PEP-2 (60 mg/3 mL)	1	M214T408	Clorprenaline	10.272	(-0.162, -0.977)	1.473
	2	M302T376	Ractopamine	8.457	(-0.147, -0.974)	3.445
	3	M396T447	Orbifloxacin	7.665	(-0.126, -0.955)	3.161
	4	M308T581	Betaxolol	6.445	(-0.099, -0.917)	-1.586
	5	M220T112	Cimaterol	4.452	(-0.059, -0.937)	1.496
	6	M365T497	Brombuterol	4.343	(-0.057, -0.922)	0.981
	7	M828T635	Josamycin	2.651	(-0.041, -0.992)	-0.165
	8	M456T425	Cefotaxime	2.221	(-0.034, -0.925)	-4.661
	9	M494T682	Glibenclamide	1.739	(-0.027, -0.966)	4.137
	10	M400T476	Difloxacin	1.436	(-0.021, -0.957)	1.497
Oasis HLB (60 mg/3 mL)	1	M266T625	Albendazole	8.787	(-0.127, -0.958)	1.258
	2	M279T200	Sulfmethazine	7.239	(-0.102, -0.989)	2.928
	3	M393T498	Sparfloxacin	5.918	(-0.087, -0.949)	1.687
	4	M370T363	Fleroxacin	3.926	(-0.062, -0.966)	0.583
	5	M352T427	Lomefloxacin	3.855	(-0.055, -0.946)	1.176
	6	M360T422	Enrofloxacin	3.108	(-0.043, -0.947)	0.853
	7	M332T406	Ciprofloxacin	2.819	(-0.035, -0.927)	1.331
	8	M304T347	Pipemidic acid	2.801	(-0.034, -0.981)	0.524
	9	M320T375	Norfloxacin	2.657	(-0.029, -0.991)	0.631
	10	M362T386	Ofloxacin	2.431	(-0.026, -0.923)	0.908
	11	M321T381	Enoxacin	2.202	(-0.023, -0.958)	1.467
	12	M271T366	Sulfamethizole	2.011	(-0.021, -0.998)	1.927
	13	M447T664	Hydrocortisone 17-valerate	1.742	(-0.019, -0.974)	1.363
	14	M363T386	Marbofloxacin	1.513	(-0.017, -0.923)	2.027
	15	M256T260	Sulfathiazole	1.231	(-0.015, -0.973)	0.28
ProElut PLS (60 mg/1 mL)	1	M233T600	Nalidixic acid	6.278	(-0.103, -0.917)	-0.77
	2	M291T360	Trimethoprim	6.142	(-0.094, -0.922)	0.465
	3	M265T334	Sulfamerazine	5.881	(-0.086, -0.937)	-1.223
	4	M267T216	Atenolol	4.912	(-0.067, -0.955)	0.117
	5	M407T350	Lincomycin	3.611	(-0.055, -0.912)	0.698
	6	M282T634	Indoprofen	3.174	(-0.048, -0.974)	-3.251
	7	M251T202	Sulfadiazine	3.154	(-0.046, -0.926)	-0.004
	8	M310T393	Nadolol	2.894	(-0.044, -0.967)	0.526
	9	M338T542	Tenoxicam	2.705	(-0.041, -0.929)	1.112
	10	M201T179	Ronidazole	2.512	(-0.038, -0.931)	0.645
	11	M332T612	Piroxicam	2.117	(-0.033, -0.956)	1.236
	12	M262T633	Flumequine	1.995	(-0.029, -0.915)	1.399
	13	M368T364	Cefaclor	1.992	(-0.029, -0.911)	1.122
	14	M348T406	Cephalexin	1.804	(-0.027, -0.966)	0.915
	15	M285T408	Sulfachloropyridazine	1.769	(-0.027, -0.938)	2.938
	16	M479T622	Triamcinolone diacetate	1.733	(-0.026, -0.959)	1.721
	17	M358T420	Danofloxacin	1.702	(-0.026, -0.932)	1.999
	18	M361T614	Cortisone	1.677	(-0.025, -0.992)	-0.165
	19	M424T302	Cefapirin	1.671	(-0.025, -0.951)	-0.052
	20	M172T166	Metronidazole	1.573	(-0.024, -0.977)	2.047
	21	M477T653	Triamcinolone acetonide 21-acetate	1.562	(-0.024, -0.954)	4.427
	22	M170T541	Ipronidazole	1.534	(-0.022, -0.931)	1.644
	23	M263T551	Cinoxacin	1.433	(-0.020, -0.976)	1.061
	24	M364T217	Cefadroxil	1.317	(-0.019, -0.954)	-0.223
	25	M454T425	Cefixime	1.309	(-0.019, -0.952)	0.2
	26	M524T568	Ceftiofur	1.218	(-0.018, -0.949)	1.569
	27	M357T644	Sulindac	1.156	(-0.017, -0.938)	2.956

Table S3 'Biomarkers' screened in positive ion mode (1 μg·L^{-1} PPCPs in reservoir water)

	28	M259T295	Sasapyrine	1.098	(-0.016, -0.947)	4.151
ProElut PLS (60 mg/3 mL)	1	M453T706	Repaglinde	6.617	(-0.102, -0.967)	1.599
	2	M512T627	Cefetamet pivoxyl	4.478	(-0.059, -0.949)	0.362
	3	M301T557	Sulfaquinoxaline	2.445	(-0.038, -0.952)	-0.587
	4	M277T551	Sulfabenzamide	1.782	(-0.026, -0.973)	1.859
	5	M336T672	Sulfanitran	1.229	(-0.016, -0.933)	3.752
ProElut PLS (100 mg/6 mL)	1	M142T190	Dimetridazole	9.211	(-0.127, -0.945)	1.579
	2	M409T692	Beclomethasone	5.515	(-0.067, -0.949)	2.827
	3	M268T345	Sulfamoxole	3.902	(-0.055, -0.943)	0.003
	4	M505T700	Betamethasone dipropionate	3.179	(-0.043, -0.947)	0.029
	5	M363T603	Hydrocortisone	2.214	(-0.032, -0.991)	-0.292
	6	M350T407	Cephradine	1.211	(-0.016, -0.978)	-2.962

Note: Mass error (ppm) = (extracted molecular weight from XCMS software - extracted molecular weight from LC-MS/MS)*10^6/extracted molecular weight from LC-MS/MS

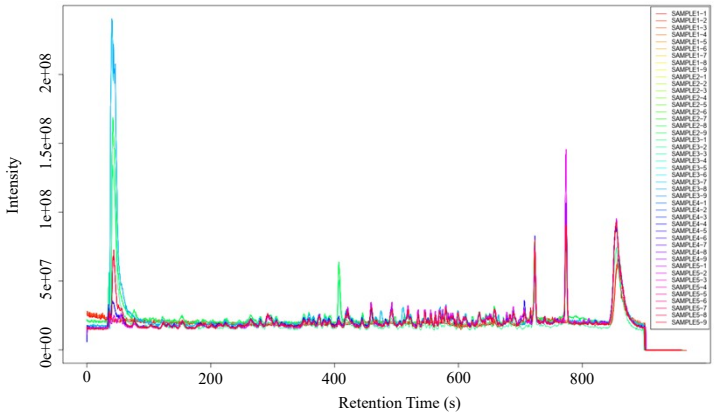

Fig. S1 Total ion chromatograms of spike reservoir water samples treated with 5 SPE columns.

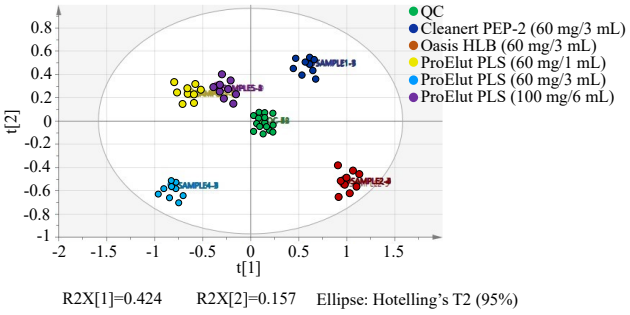

Fig. S2 Score plots of PCA of spike reservoir water sample groups.

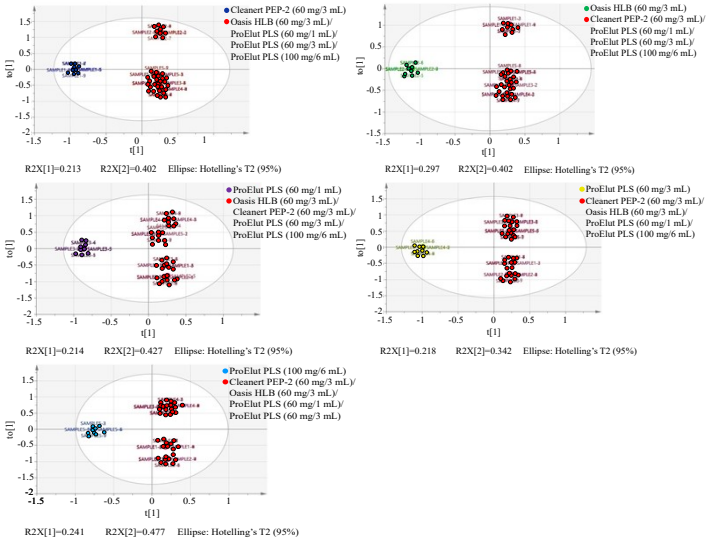

Fig. S3 Score plots of OPLS-DA of spike reservoir water sample groups.

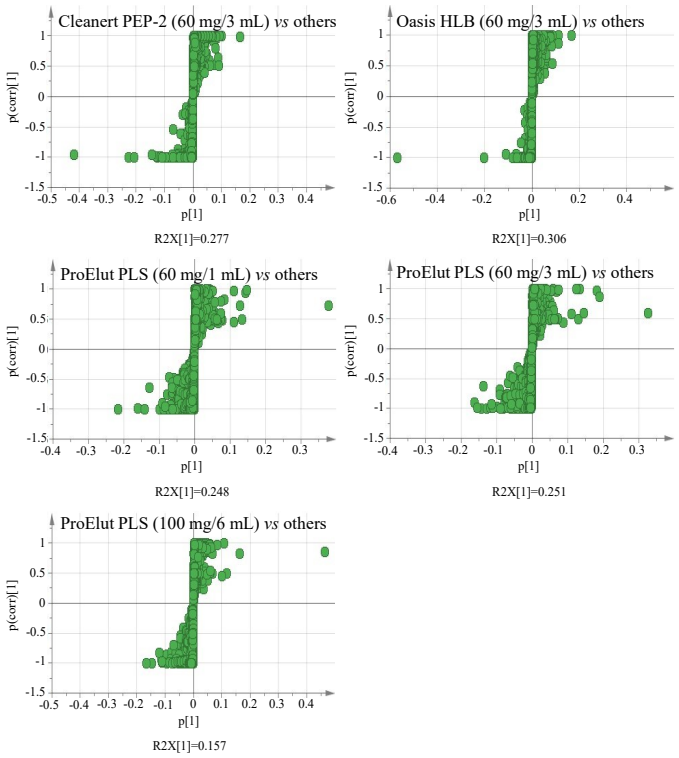

Fig. S4 S-plot plots of spike reservoir water sample groups.

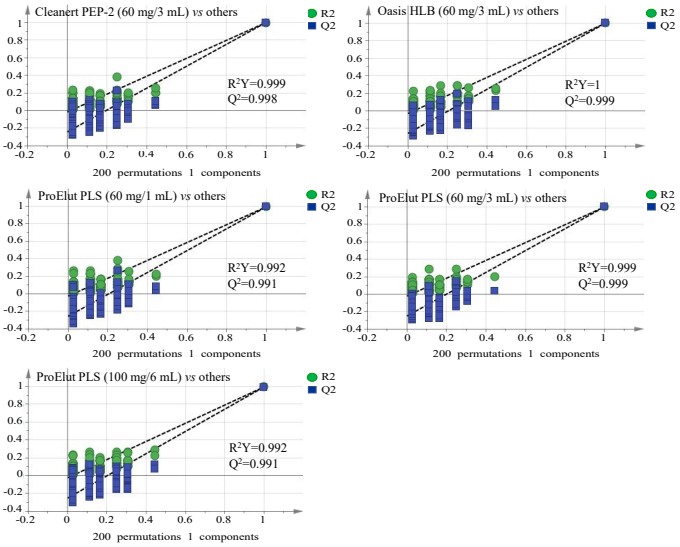

Fig. S5 Permutation plots of spike reservoir water sample groups.