Supporting Information

Determination and distribution of pesticides and antibiotics in agricultural soils from northern China

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Table S1. The gradient elution program for 47 pesticides analysis

Time (min)	Methanol (%)	0.1% formic acid water (%)	Flow rate (mL/min)
0	1	99	0.2
0.5	1	99	0.2
2	30	70	0.2
4	30	70	0.2
8	70	30	0.2
10	70	30	0.2
11	99	1	0.2
16	99	1	0.2
17.5	1	99	0.2
25	1	99	0.2

Table S2. The gradient elution program for 10 antibiotics analysis

Time (min)	Methanol (%)	0.1% formic acid water (%)	Flow rate (mL/min)
0	5	95	0.3
1	5	95	0.3
5	25	75	0.3
8.5	90	10	0.3
9.5	90	10	0.3

10	5	95	0.3
13	5	95	0.3

Table S3. HPLC-MS/MS parameters and validation results (calibration curves, R^2, LOD, recoveries and RSD) of 47 pesticides

Category	Compounds	RT(min)	Fragmentor(V)	Precursor ion	Product ion	Collision energy (V)	Calibration curve (R^2)	LOD µg/kg	Recovery, %(RSD, %)		
									0.005 mg/kg	0.05 mg/kg	0.5 mg/kg
Amides/anilines	Acetochlor	16.15	80	270.2	148.2* 133.3	15 30	y = 92752x - 664.36 (0.9993)	0.03	85(10)	87(12)	81(8)
	Boscalid	15.50	140	343.2	307.2* 271.0	20 35	y = 434522x – 3297 (0.9997)	0.03	82(10)	72(4)	72(2)
	Butachlor	17.42	80	312.2	238.1* 162.0	10 20	y = 352578x - 1295.5 (0.9998)	1.00	94(10)	95(6)	72(3)
	Cloransulam-methyl	13.73	80	430.0	370.0* 306.0	20 25	y = 290085x - 4415.3 (0.9957)	0.04	80(18)	79(7)	84(3)
	Diflufenican	17.08	110	395.0	266.1* 246.0	20 30	y = 255956x + 892.09 (0.9967)	0.13	93(11)	76(14)	75(2)
	Mefenacet	15.92	90	299.1	148.2* 120.0	4 10	y = 1E+06x + 1146.4 (1.0000)	0.05	76(11)	74(2)	72(5)
	Metolachlor	16.25	95	284.2	176.4* 253.2	12 12	y = 531672x – 4288 (0.9992)	0.16	99(13)	75(6)	78(3)
	Penoxsulam	13.91	150	484.0	195.1* 164.0	30 40	y = 334217x – 4208 (0.9969)	0.04	75(4)	83(8)	87(3)
	Pretilachlor	17.11	100	312.2	252.2* 176.2	10 15	y = 4E+06x + 25679 (0.9980)	0.48	73(3)	72(1)	75(3)
	Pyrimethanil	13.95	120	200.2	107.0* 183.1	25 25	y = 2E+06x – 17585 (0.9996)	0.85	78(9)	71(4)	73(4)
	Thifluzamide	16.33	160	529.0	488.9* 168.0	30 25	y = 27724x + 554.84 (0.9944)	1.00	95(8)	85(13)	85(7)
Anilinopyrimidine	Cyprodinil	15.52	120	226.0	93.0* 108.0	40 30	y = 2E+06x – 28570 (0.9978)	0.22	73(5)	75(3)	72(1)
Aryloxyphenoxy-propionates	Fenoxaprop-p-ethyl	17.27	100	362.2	288.1* 244.2	15 20	y = 1E+06x + 15727 (0.9966)	0.24	84(14)	71(1)	75(3)

Azoles	Difenoconazole	17.00	155	406.0	251.0* 337.0	25 15	y = 4E+06x + 17038 (0.9991)	0.06	78(6)	72(3)	73(2)
	Epoxiconazole	16.30	120	330.1	121.1* 141.1	20 20	y = 3E+06x – 20987 (0.9997)	0.15	73(4)	73(2)	75(4)
	Hexaconazole	16.75	120	314.1	70.1* 158.9	20 35	y = 4E+06x – 25413 (0.9995)	0.05	73(6)	72(3)	72(2)
	Paclobutrazol	15.59	100	294.2	70.0* 125.0	15 25	y = 5E+06x – 84165 (0.9963)	0.10	76(7)	71(2)	73(3)
	Propiconazole	16.68	70	342.2	158.9* 69.1	30 20	y = 432918x - 6197.3 (0.9971)	0.05	75(12)	71(3)	73(2)
	Tebuconazole	16.61	100	308.2	70.0* 125.0	25 25	y = 6E+06x – 30812 (0.9997)	0.06	73(7)	71(3)	73(3)
	Tricyclazole	12.40	145	190.0	163.0* 136.0	25 30	y = 2E+06x - 9311.1 (0.9997)	0.02	84(7)	72(4)	74(2)
Benzimidazole	Carbendazim	8.52	80	192.1	160.1* 132.1	15 20	y = 1E+06x + 9706.3 (0.9987)	0.05	80(4)	72(6)	73(5)
	Thiabendazole	9.31	145	202.1	175.1* 131.0	25 30	y = 539088x - 4774.8 (0.9986)	0.25	82(8)	76(6)	73(5)
Carbamate	Carbofuran	11.42	120	222.3	165.1* 123.1	5 20	y = 1E+06x + 684.75 (0.9999)	0.25	87(16)	94(4)	91(4)
	Methomyl	9.02	80	163.2	88.1* 106.1	5 10	y = 199924x - 2784.3 (0.9989)	0.25	79(11)	84(11)	85(7)
	Pirimicarb	10.85	120	239.2	72.0* 182.2	20 15	y = 3E+06x – 39216 (0.9982)	0.50	90(9)	73(8)	75(3)
Neonicotinoids	Acetamiprid	11.43	120	223.2	126.0* 56.0	15 15	y = 336940x - 199.36 (0.9998)	0.25	99(4)	82(9)	80(5)
	Clothianidin	10.86	80	250.2	169.1* 132.0	10 15	y = 94329x - 549.9 (0.9999)	1.00	89(10)	84(8)	84(5)
	Imidacloprid	10.70	80	256.1	175.1* 209.1	10 10	y = 158852x + 56816 (0.9929)	0.06	87(6)	92(4)	87(4)
	Thiamethoxam	9.18	80	292.1	211.2* 181.1	10 20	y = 110844x – 2060 (0.9959)	0.79	73(15)	91(7)	81(6)
Organochlorine/org	Bentazone	17.46	80	240.3	162.1*	10	y = 284608x - 316.07	0.91	83(7)	74(3)	73(3)

anophosphate					147.1	20	(0.9999)				
	Chlorpyrifos	17.62	100	350.0	198.0* 79.0	20 35	y = 136901x - 914.24 (0.9996)	1.00	78(13)	78(5)	71(4)
	Pyridaben	18.15	100	365.1	147.1* 309.1	20 20	y = 5E+06x – 23464 (0.9998)	0.07	83(9)	74(3)	73(2)
	Spirodiclofen	17.89	70	411.1	313.1* 295.1	5 25	y = 555772x - 3350.4 (0.9998)	0.01	78(10)	72(6)	73(2)
Oxazinone	Oxaziclomefone	17.24	80	376.1	190.1* 161.1	10 25	y = 3E+06x + 21565 (0.9964)	0.08	74(9)	74(2)	75(2)
Strobilurin	Azoxystrobin	15.18	120	404.0	372.0* 344.1	10 15	y = 2E+06x – 10668 (0.9999)	0.27	75(10)	72(4)	75(5)
	Kresoxim-methyl	16.54	100	314.0	222.1* 193.9	8 30	y = 152585x + 1327.6 (0.9987)	1.00	91(14)	72(7)	77(3)
	Picoxystrobin	16.45	80	368.1	145.0* 205.0	12 4	y = 4E+06x - 5539.2 (0.9999)	0.06	77(10)	72(2)	76(4)
	Pyraclostrobine	16.83	90	387.8	163.1* 149.0	20 30	y = 1E+06x + 3925.2 (0.9994)	0.05	80(8)	73(5)	75(3)
Substituted urea	Isoproturon	14.38	120	207.2	72.0* 165.1	15 15	y = 4E+06x – 14461 (0.9999)	0.11	93(13)	76(2)	82(3)
Sulfonylurea	Halosulfuron-methyl	16.43	120	434.8	181.9* 402.7	15 4	y = 432918x - 6197.3 (0.9971)	0.12	82(15)	81(7)	79(2)
	Nicosulfuron	13.40	120	411.0	182.0* 213.0	19 19	y = 689475x - 6246.3 (0.9987)	0.05	9(17)	11(16)	12(4)
	Pyrazosulfuron-ethyl	16.21	102	415.0	182.0* 139.0	15 15	y = 1E+06x – 23215 (0.9942)	0.02	73(10)	75(6)	73(3)
Thiadiazine	Buprofezin	17.16	120	306.2	116.0* 201.0	10 15	y = 7E+06x + 47942 (0.9988)	0.04	77(8)	71(2)	73(3)
Triazine	Atrazine	14.29	120	216.0	174.2* 132.0	15 20	y = 5E+06x – 67935 (0.9974)	0.11	73(9)	74(5)	79(2)
	Prometryn	14.21	120	242.2	158.1* 200.1	20 20	y = 1E+07x – 159257 (0.9980)	0.24	76(11)	72(2)	75(3)
Triazinone	Pymetrozine	1.08	100	218.1	105.1* 78.0	20 40	y = 277164x + 442.31 (0.9992)	0.75	50(10)	39(13)	45(9)

Triazolinones	Sulfentrazone	13.61	130	387.1	307.1* 273.0	20 30	y = 52960x - 678.81 (0.9970)	1.00	92(10)	86(11)	77(7)	

Note: The product ion "*" indicates that it is the quantification ion, and the other is the confirmatory ion.

Table S4. HPLC-MS/MS parameters and validation results (calibration curves, R^2, LOD, recoveries and RSD) of 10 antibiotics

Category	Compounds	RT (min)	Fragmentor(V)	Precursor ion	Product ion	Collision energy (V)	Calibration curve (R^2)	LOD µg/kg	Recovery, %(RSD, %)			
									0.01 mg/kg	0.05 mg/kg	0.1 mg/kg	0.5 mg/kg
Tetracyclines	Chlortetracycline	10.1	115	479.2	260.2* 303.2 286.2	60 40 60	y = 42420x - 5.1174 (0.9989)	1.20	75(11)	89(8)	73(3)	76(3)
	Doxycycline	10.6	120	445.2	201.0* 186.9 252.2	45 50 50	y = 54499x + 96.08 (0.9994)	1.00	86(8)	89(10)	70(4)	71(2)
	Oxytetracycline	8.9	120	461.2	201.1* 283.1 268.3	40 45 55	y = 70010x + 119.87 (0.9997)	1.00	94(15)	96(10)	87(17)	72(10)
	Tetracycline	8.8	120	445.2	154.2* 241.1 267.2	25 45 40	y = 147737x + 152.82 (0.9996)	0.75	78(6)	99(10)	73(4)	73(3)
Macrolids	Erythromycin	11.1	130	734.5	158.1* 116	30 50	y = 493369x - 936.01 (0.9993)	0.04	39(6)	51(9)	49(6)	53(5)
	Roxithromycin	11.5	135	837.6	158.1* 116	35 50	y = 662896x + 1170.9 (0.9998)	0.01	38(13)	40(4)	37(7)	42(7)
Sulfonamides	Sulfadimethoxine	10.6	110	311.2	156.2* 108.1 173.1	20 30 30	y = 717419x + 1232.1 (0.9997)	0.10	91(2)	92(3)	94(2)	82(2)
	Sulfamerazine	6.9	110	265.2	108.1* 172 156	25 10 10	y = 230172x + 14.465 (0.9993)	1.15	108(3)	85(5)	76(5)	81(2)
	Sulfameter	8.4	110	281.2	108.2*	25	y = 137677x - 62.506	2.00	77(5)	71(3)	77(6)	77(4)

				126.2	25	(0.9996)					
				108.1*	20						
Sulfamethoxazole	9.4	100	254.2	146.1	15	y = 234875x + 229.41 (0.9997)	0.57	84(11)	87(4)	84(3)	80(1)
				160.3	15						

Note: “*” indicates the quantification ion.

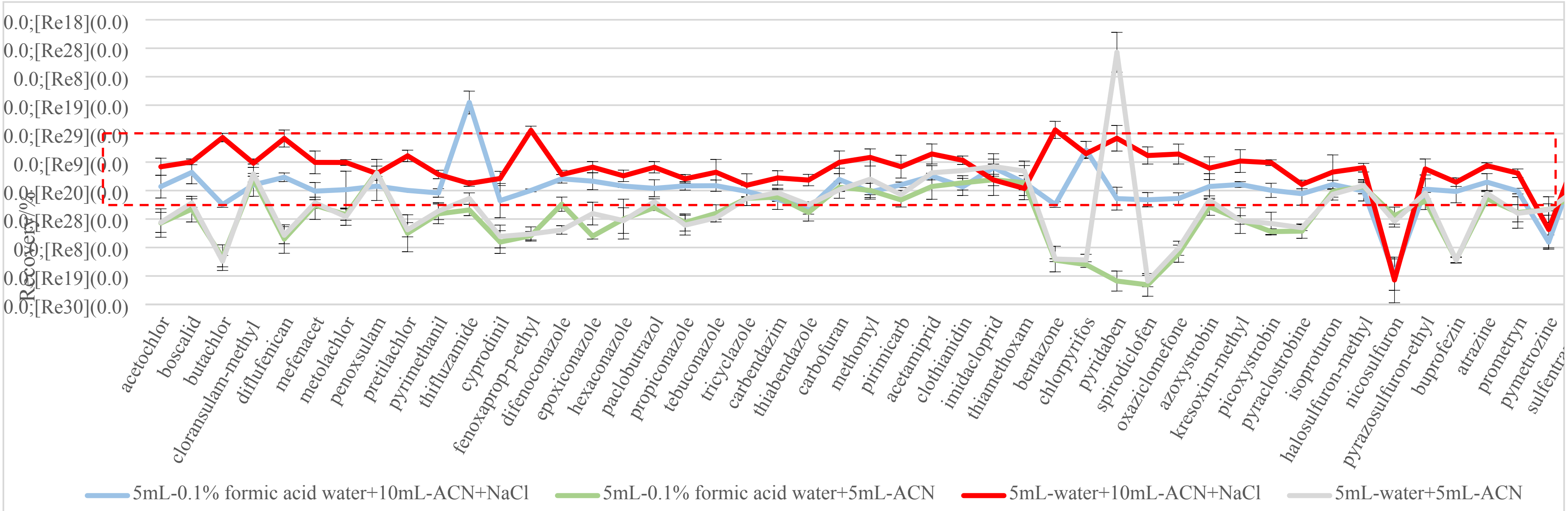

Figure S1. Recoveries of pesticides with different extraction conditions. "5ml-0.1% formic acid water+10ml-ACN+NaCl" is 10.0 g of soil sample with 5 mL 0.1% formic acid water, 10 mL acetonitrile, and 3 g NaCl.

It can be seen from the figure S1 that the recovery was improved with NaCl as salting out under the same conditions, and the recovery was improved with water extraction under the same conditions.

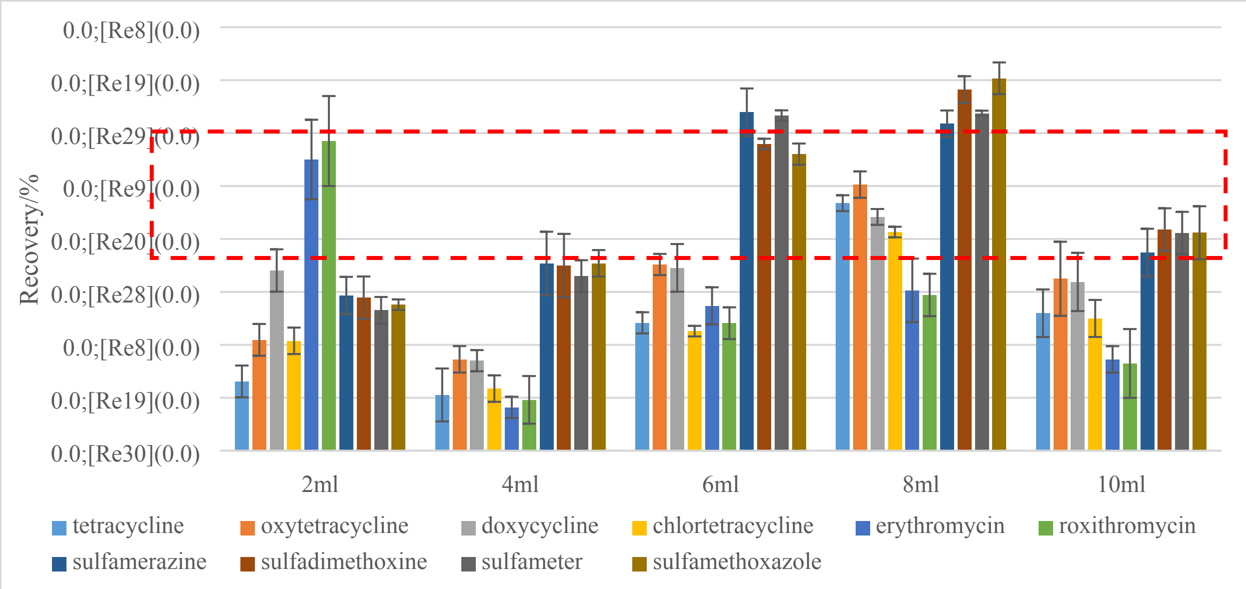

Figure S2. Recoveries of antibiotics with different extraction solvent volume (extraction time was 30 min)

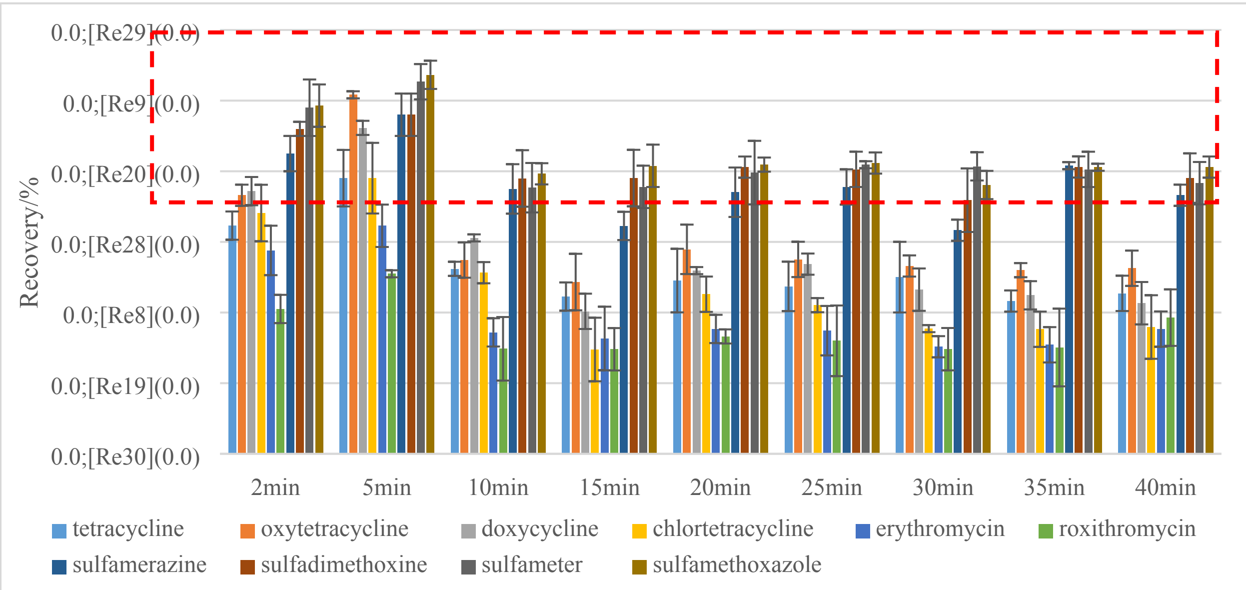

Figure S3. Recoveries of antibiotics with different extraction time (extraction solvent volume was 8mL)

Figures S4-6 were results of the purification effects of PAX that explored at different dosages and in different roles. First, different PAX dosages were evaluated. 1 mL of 0.5 mg/L methanol/EDTA-McIlvaine (v/v=1/1) standard solution was added to 25, 50, 80, 100, and 150 mg PAX respectively. Each sample was vortexed for 30 seconds, then 1 mL of supernatant was filtered through a 0.22 μm organic filter membrane after centrifugation (10000 rpm) for 1 min. Considering that PAX cannot only absorb impurities as a cleaner, but also adsorb the target compounds as an adsorbent. Therefor 80 mg of PAX was selected to optimize eluent in the next step. 1 mL of 0.5 mg/L methanol/EDTA-McIlvaine (v/v=1/1) standard solution was placed into a 2 mL centrifuge tube with 80 mg PAX, vortexed, centrifuged, and 1 mL of supernatant was filtered through a 0.22 μm filter membrane. The 1 mL of supernatant was "up-without-eluted". The PAX adsorbent layer was eluted with different volume ratios of 1 mL methanol/water, vortexed, and after centrifugation the supernatant was filtered through the filter membrane for analysis. These supernatants were "down-'solvent'". The results showed that the recoveries of the 10 antibiotics were still low (Fig. S5). An experiment was then conducted to optimize the solvent for activation. 80 mg PAX was weighed and activated with 1 mL of methanol, water, methanol/water (v/v=6/4), water after methanol, and methanol after water, respectively, then each sample was vortexed, centrifuged at 10000 rpm, and the supernatant was discarded. 1 mL 0.5 mg/L methanol/EDTA-McIlvaine (v/v=1/1) standard solution was then added, and each sample was vortexed, centrifuged, and the supernatant from each sample was filtered through a 0.22 μm filter membrane. The supernatant of un-activated PAX sample and no clean-up sample were also made for comparison. The results showed that the recovery of activated solvent with methanol performed best, but the four sulfonamide antibiotics had low recovery (Fig. S6). Only two macrolides display a lower recovery rate without cleaning-up, while four sulfonamides have a lower recovery rate with methanol-activated cleaning. Furthermore, skipping the cleaning-up step was relatively quick, convenient, and economical. Therefore, the decision was taken not to go through the cleaning-up process.

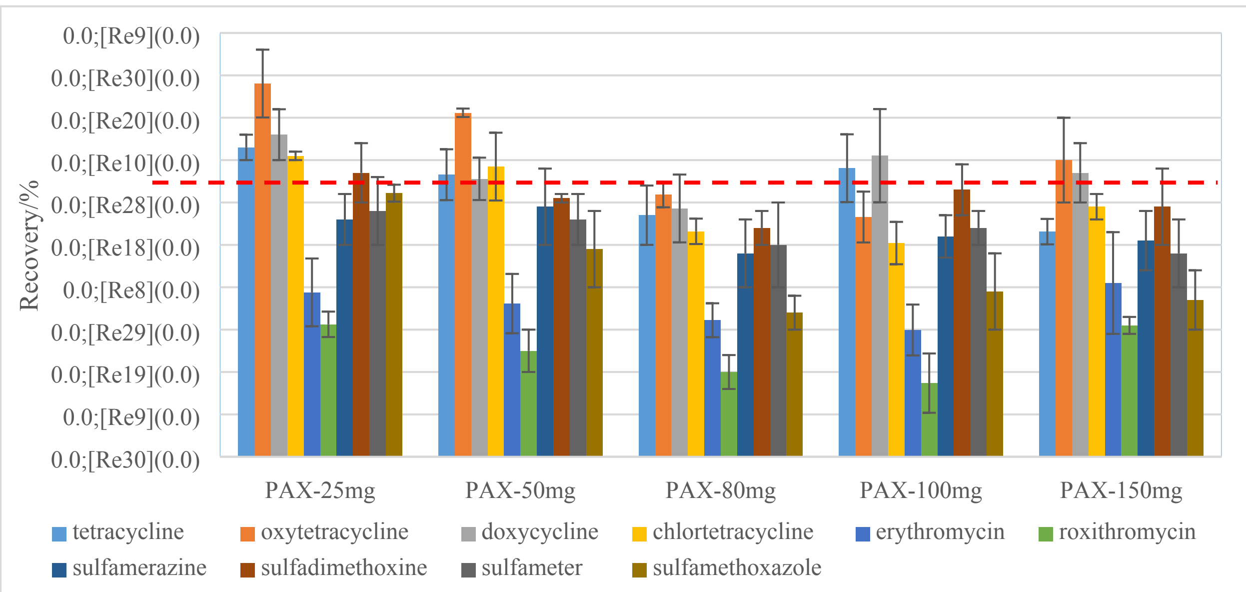

Figure S4. Recoveries of antibiotics with different amount of PAX

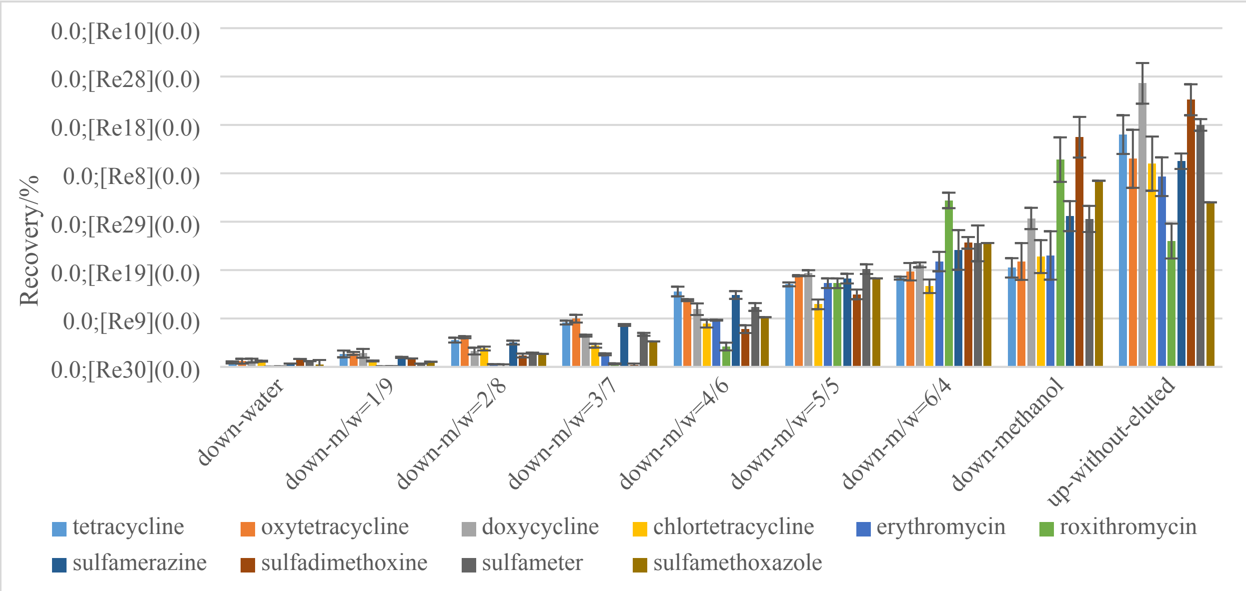

Figure S5. Comparison of recoveries of supernatant sample and different eluent

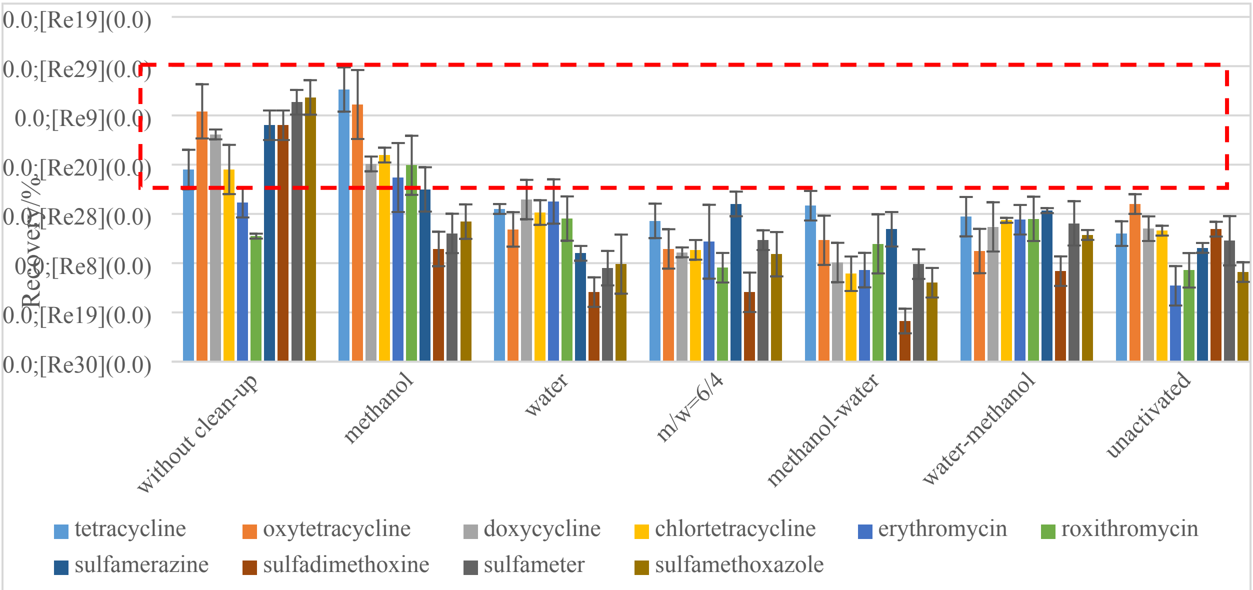

Figure S6. Comparison of recoveries of antibiotics with different solvent activation and no clean-up