SUPPLEMENTARY MATERIAL

Quality Control of Emerging Contaminants in Marine Aquaculture Systems by Spot Sampling-Optimized Solid Phase Extraction and Passive Sampling

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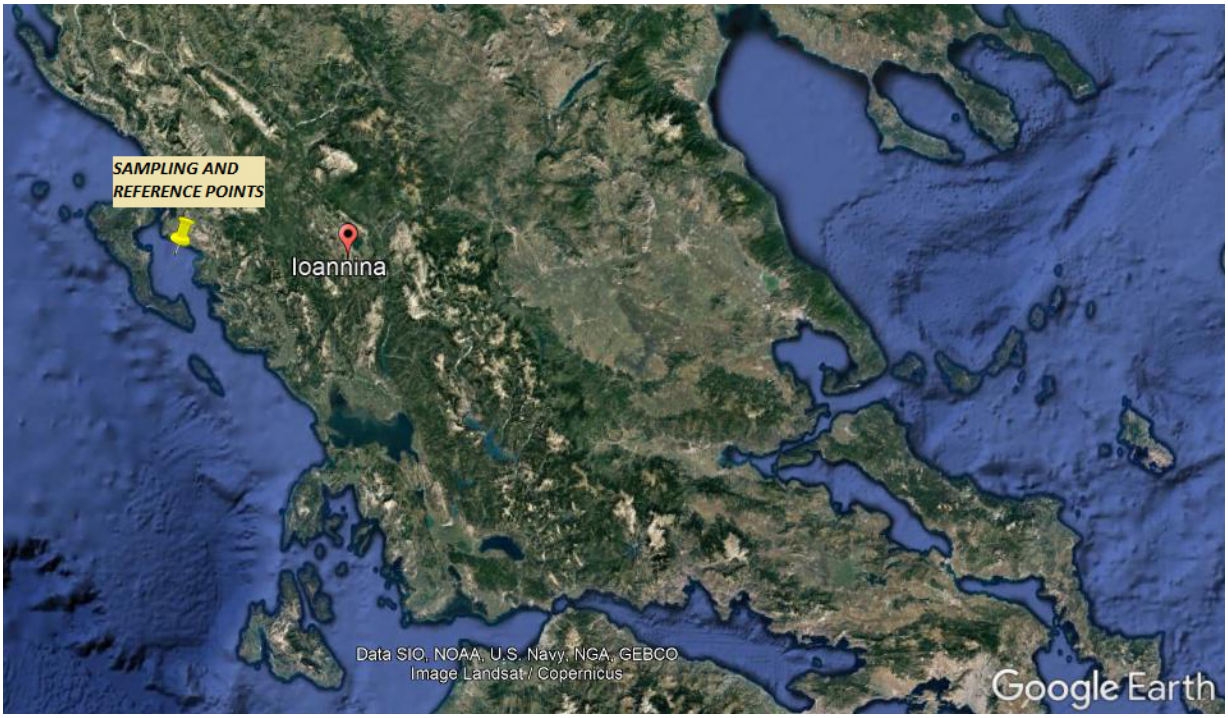

Figure S1. Sampling Location

Table S1. Solid phase extraction protocols tested for pesticides and pharmaceutical compounds efficient removal from waters.

	Pesticides			**Pharmaceuticals**	
Protocols	***HLB1***	***HLB2***	***HLB3***	***HLB4***	***HLB5***
Sample pH		No adjustment		pH 3–3.5	pH3–3.5
Na_2EDTA addition 5% w/v	-	-	5mL	5mL	-
Activation solvents	5mL MeOH, 5mL H_2O	6mL MeOH, 6mL H_2O	5mL MeOH, 5mL H_2O	5mL MeOH, 5mL H_2O acidified with formic acid	5mL MeOH, 5mL H_2O acidified with formic acid
Wash solvent	5mL H_2O	6mL H_2O	5mL H_2O	5mL H_2O	5mL H_2O with 20% MeOH+2% acetic acid
Elution solvent	2x5 mL MeOH	3mL Dichloromethane 3mL Hexane 3mL Acetone	2 × 5 mL MeOH	2 × 5 mL MeOH	2 × 5 mL MeOH+2% acetic acid
Injection solvent	H_2O:MeOH (90:10)+0.1% formic acid	H_2O:MeOH (90:10)+0.1% formic acid	H_2O:MeOH (90:10)	H_2O:MeOH (90:10)+0.1% formic acid	H_2O:MeOH (90:10)

Table S2. Detection parameters for full MS/dd-MS^2 analysis of pesticides.

			Orbitrap MS				Orbitrap dd-MS^2 [b]
Compound	**t_R (min)**	**Elemental Formula**	**Theoretical Mass (m/z)**	**Experimental Mass (m/z)**	**Mass Accuracy Δ(ppm)**	**NCE [a] (%)**	**Fragment Ions**
azamethiphos	5.18	$C_9H_{11}ClN_2O_5PS^+$	324.9809	324.9811	−0.094	30	127.9899
azoxystrobin	5.79	$C_{22}H_{18}N_3O_5^+$	404.1241	404.1244	0.700	30	372.0984
boscalid	5.94	$C_{18}H_{13}Cl_2N_2O^+$	343.0399	343.0402	0.773	40	307.0636
malathion	6.02	$C_{10}H_{20}O_6PS_2^+$	331.0433	331.0437	1.079	30	285.0017
irgarol	6.15	$C_{11}H_{20}N_5S^+$	254.1434	254.1437	0.907	30	198.0811
tebufenozide	6.30	$C_{22}H_{28}N_2O_2^+$	353.2224	353.2226	0.702	30	133.0649
pirimiphos-methyl	6.56	$C_{11}H_{20}N_3O_3PS^+$	306.1036	306.1038	0.827	40	278.0728
abamectin	7.70	$C_{48}H_{72}O_{14}Na^+$	895.4814	895.4827	1.382	30	751.4027

[a] NCE; Normalized Collision Energy. [b] dd-MS^2;data dependent- MS^2.

Table S3. Detection parameters for full MS/dd-MS² analysis of pharmaceuticals.

			Orbitrap MS				Orbitrap dd-MS² [b]
Compound	t_R(min)	Elemental Formula	Theoretical Mass (m/z)	Experimental Mass (m/z)	Mass Accuracy Δ(ppm)	NCE [a] (%)	Fragment Ions
atenolol	3.35	$C_{14}H_{23}N_2O_3^+$	267.1703	267.1705	0.802	30	225.1236
cimetidine	3.36	$C_{10}H_{17}N_6S^+$	253.1230	253.1232	1.099	30	159.0697
paracetamol	3.43	$C_8H_{10}NO_2^+$	152.0706	152.0706	−0.593	35	110.0597
sulfadiazine	3.45	$C_{10}H_{11}N_4O_2S^+$	251.0597	251.0598	0.281	35	156.0113
olanzapine	3.48	$C_{17}H_{21}N_4S^+$	313.1481	313.1482	0.254	40	256.0906
sulfapyridine	3.56	$C_{11}H_{12}N_3O_2S^+$	250.0645	250.0648	1.264	30	156.0115
amisulpride	3.58	$C_{17}H_{28}N_3O_4S^+$	370.1795	370.1797	0.269	40	242.0484
trimethoprim	3.61	$C_{14}H_{19}N_4O_3^+$	291.1462	291.1454	0.617	30	230.1164
sulfamethazine	3.74	$C_{12}H_{15}N_4O_2S^+$	279.0910	279.0915	1.351	30	204.0440
sulfamethoxazole	3.82	$C_{10}H_{12}N_3O_3S^+$	254.0594	254.0597	0.135	30	195.0919
mirtazapine	3.83	$C_{17}H_{20}N_3^+$	266.1652	266.1652	0.203	30	156.0113
phenazone	3.90	$C_{11}H_{13}N_2O^+$	189.1022	189.1023	0.267	40	161.1074
risperidone	3.90	$C_{23}H_{28}FN_4O_2^+$	411.2191	411.2192	0.193	30	191.1183
bupropion	4.00	$C_{13}H_{19}ClNO^+$	240.1150	240.1151	0.444	30	184.0526
venlafaxine	4.05	$C_{17}H_{28}NO_2^+$	278.2115	278.2115	0.219	35	260.2009
citalopram	4.07	$C_{20}H_{22}FN_2O^+$	325.1711	325.1710	0.170	20	262.1027
oxolinic acid	4.10	$C_{13}H_{12}NO_5^+$	262.0710	262.0711	0.538	40	244.0606
haloperidol	4.14	$C_{21}H_{24}ClFNO_2^+$	376.1474	376.1477	0.864	30	165.0711
quetiapine	4.18	$C_{21}H_{26}N_3O_2S^+$	384.1740	384.1743	0.679	20	191.1055
paroxetine	4.30	$C_{19}C_{21}FNO_3^+$	330.1500	330.1501	0.323	40	192.1185
amitriptyline	4.43	$C_{20}H_{24}N^+$	278.1903	278.1905	0.822	35	233.1300
fluoxetine	4.49	$C_{17}H_{19}F_3NO^+$	310.1413	310.1418	1.485	20	148.1122
carbamazepine	4.50	$C_{15}H_{13}N_2O^+$	237.1022	237.1023	0.789	30	194.0966
sertraline	4.60	$C_{17}H_{18}Cl_2N^+$	306.0811	306.0810	1.008	30	158.9758
alprazolam	4.74	$C_{17}H_{14}ClN_4^+$	309.0902	309.0903	0.882	30	281.0717
ketoprofen	4.84	$C_{16}H_{15}O_3^+$	255.1016	255.1019	1.192	20	209.0959
bezafibrate	4.94	$C_{19}H_{21}ClNO_4^+$	362.1154	362.1160	1.582	30	316.1098
diazepam	5.09	$C_{16}H_{14}ClN_2O^+$	285.0789	285.0793	1.389	40	257.0844
budesonide	5.38	$C_{25}H_{35}O_6^+$	431.2428	431.2432	0.916	20	413.2321

[a] NCE; Normalized Collision Energy. [b] dd-MS²;data dependent- MS².