Supplementary Information (SI) for RSC Advances.

In situ analysis of heavy metals and halogenated compounds in reclaimed water using novel electrospray ionization combined with plasma ionization linear ions trap mass spectrometry

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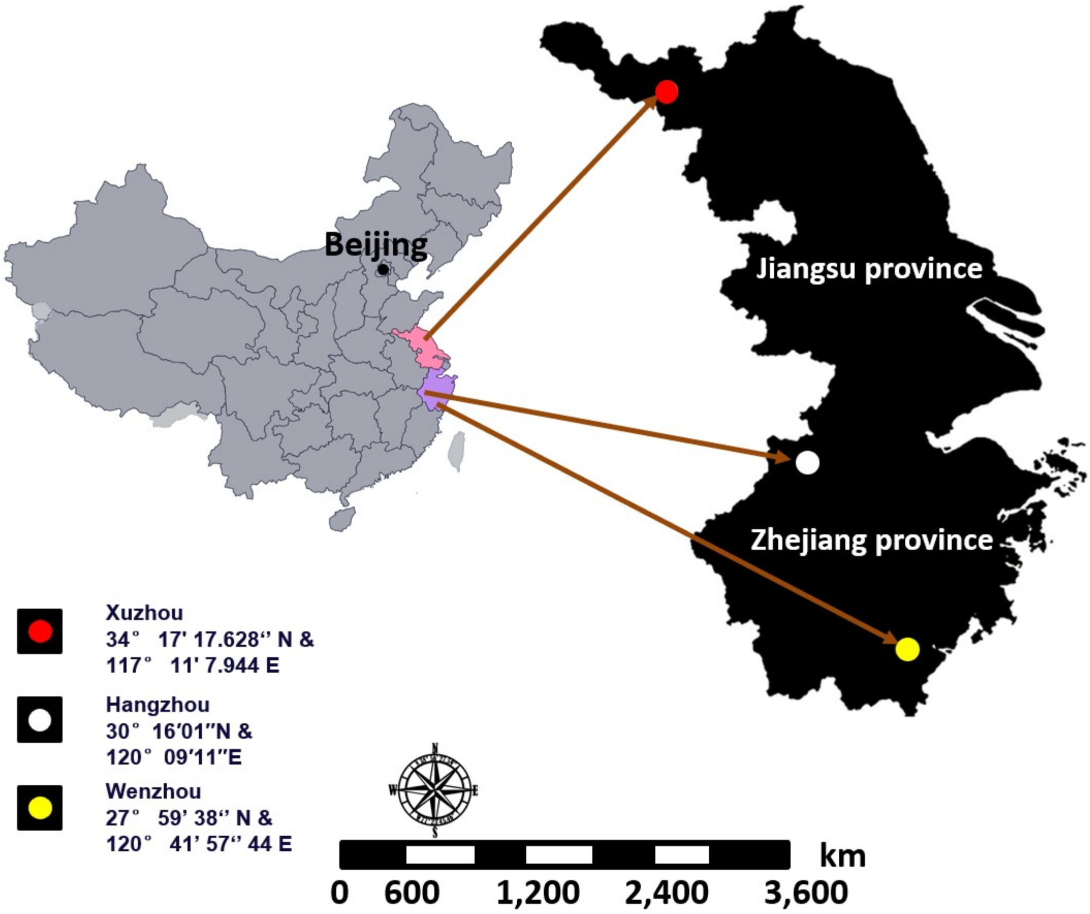
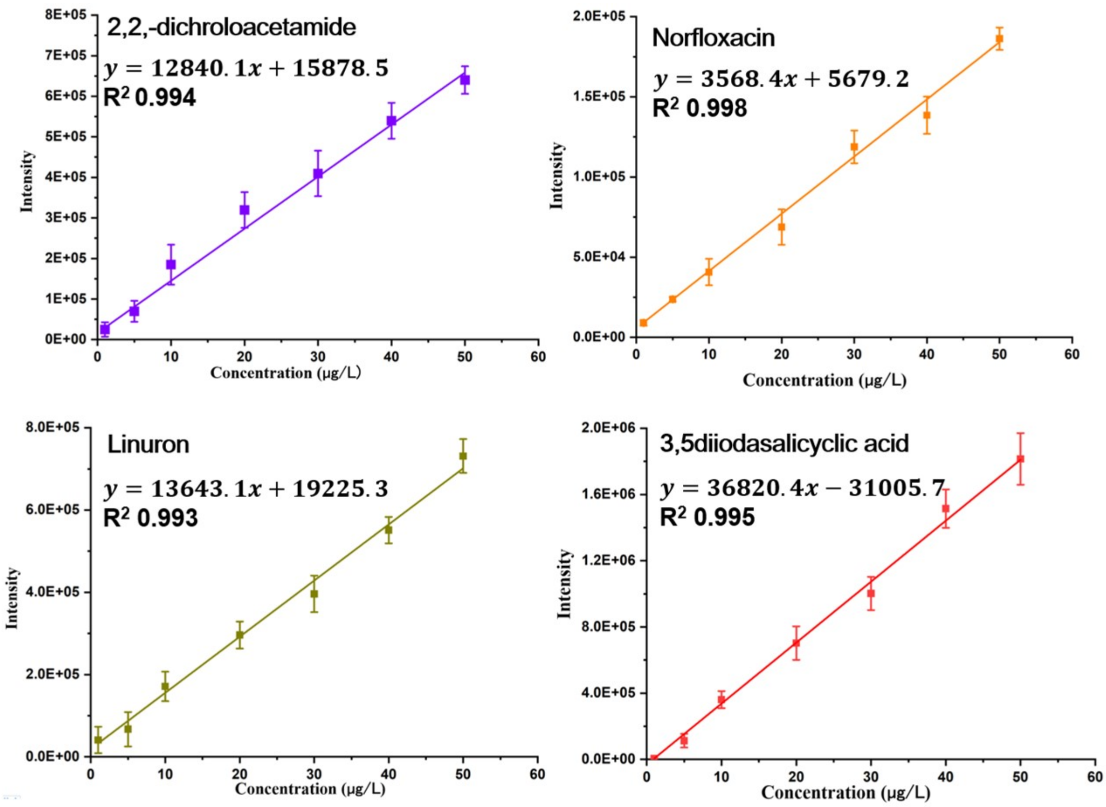


Figure S1 Map of the study area: Xuzhou, Hangzhou, and Wenzhou cities, China



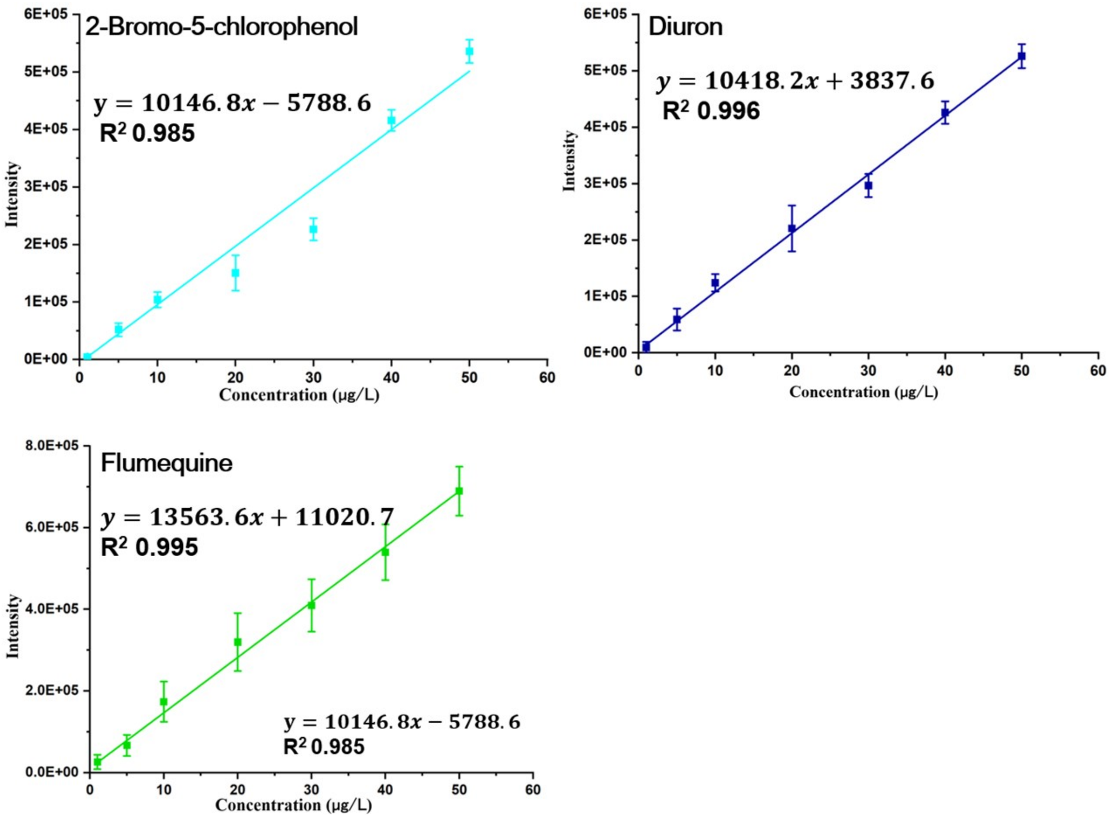


Figure S2. Calibration curve for H-compounds, including 2,2-dichloroacetamide, norfloxacin, linuron, 3,5-diiodosalicylic acid, 2-bromo-5-chlorophenol, diuron, and flumequine. Each compound's response was measured across a range of concentrations to establish linearity and sensitivity, with calibration curves constructed by plotting peak intensity versus concentration.

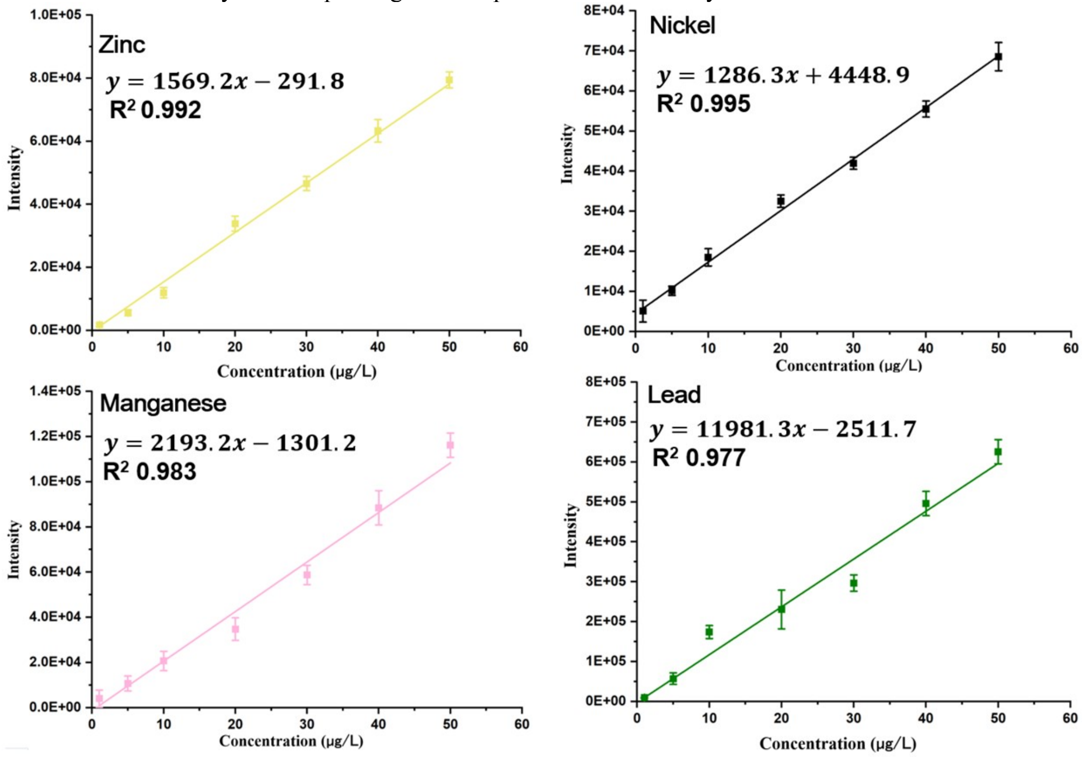
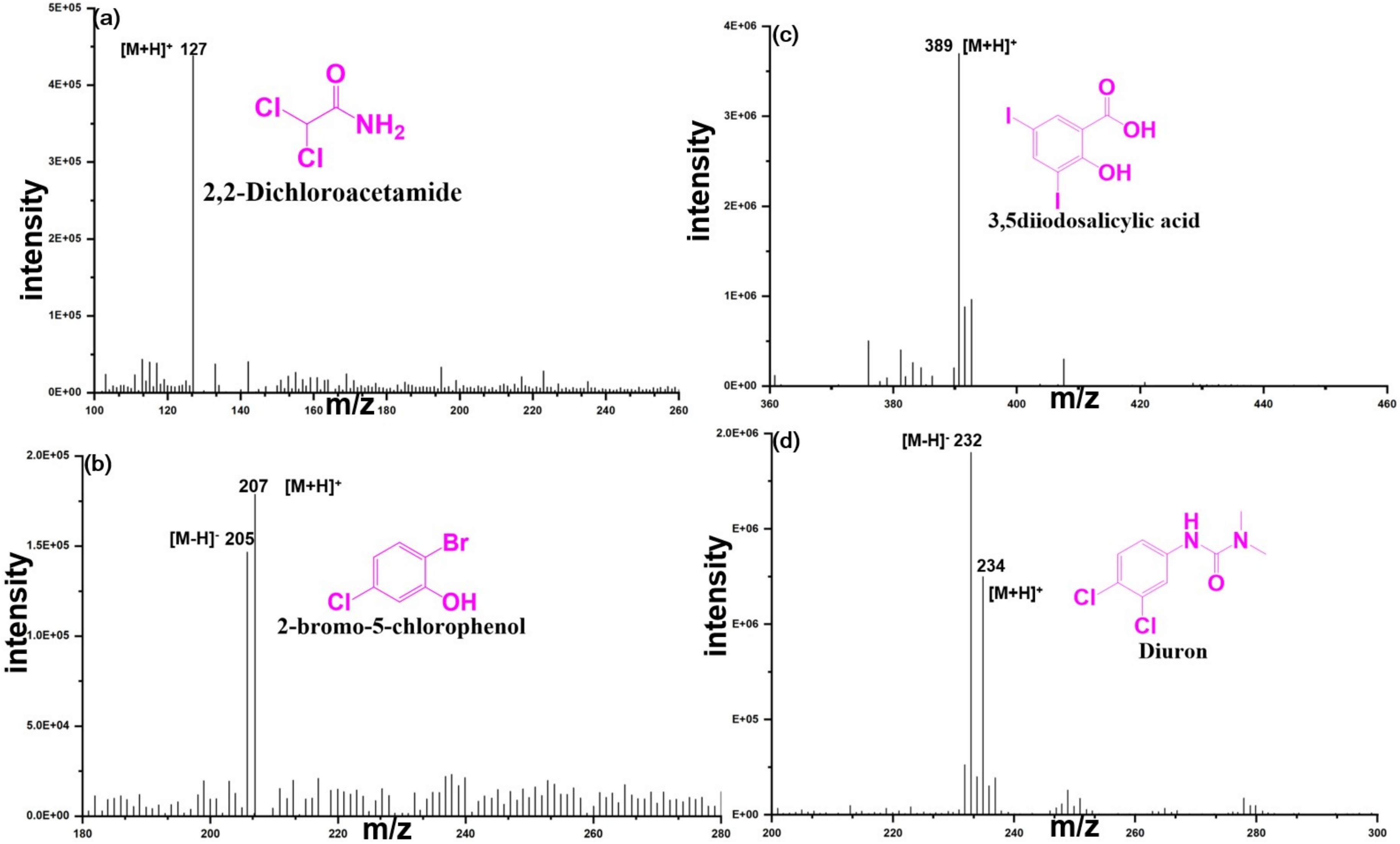
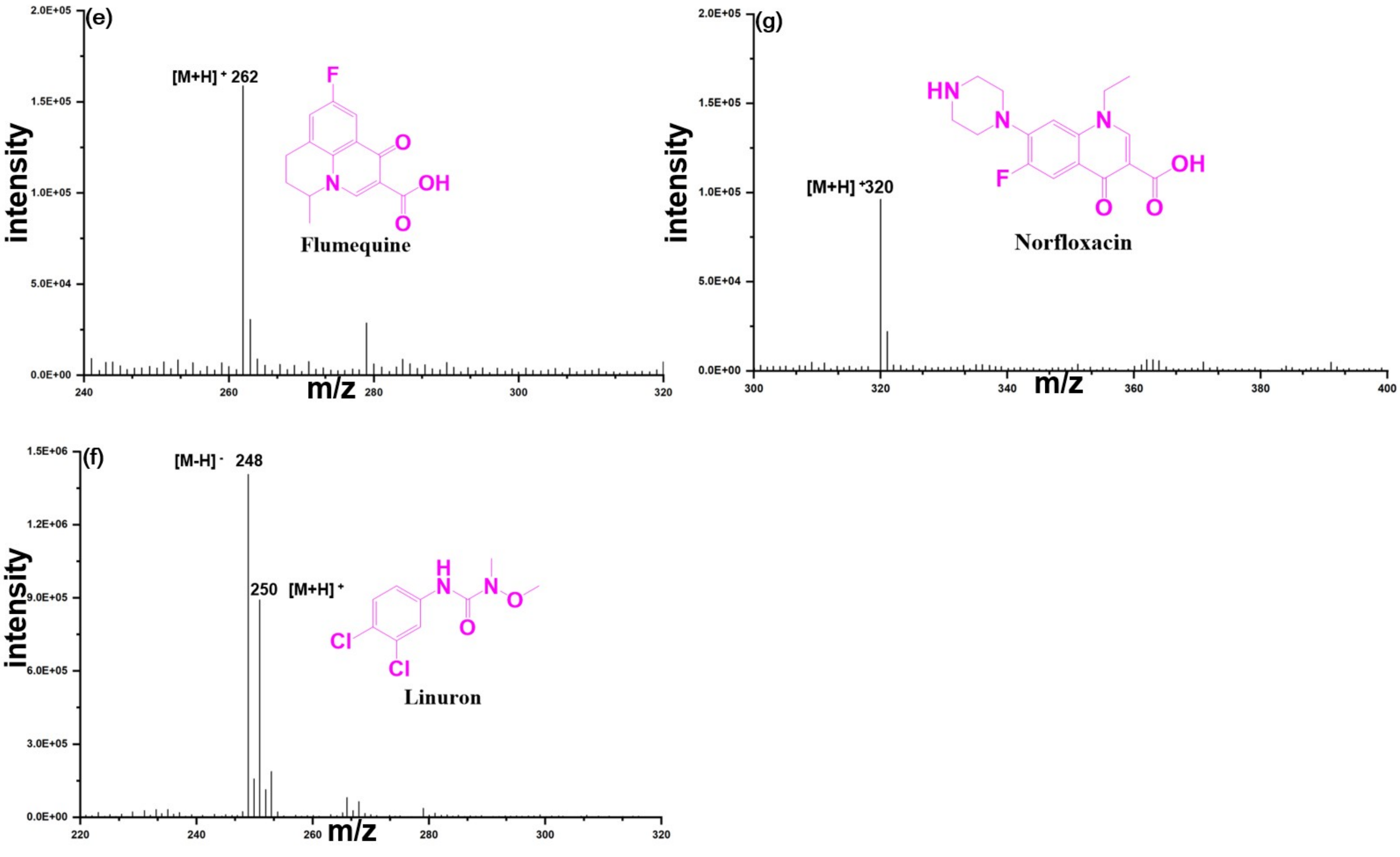


Figure S3. Calibration curves for heavy metals, including zinc, manganese, nickel, and lead. Each metal's response was measured across a series of standard concentrations to evaluate linearity and sensitivity.

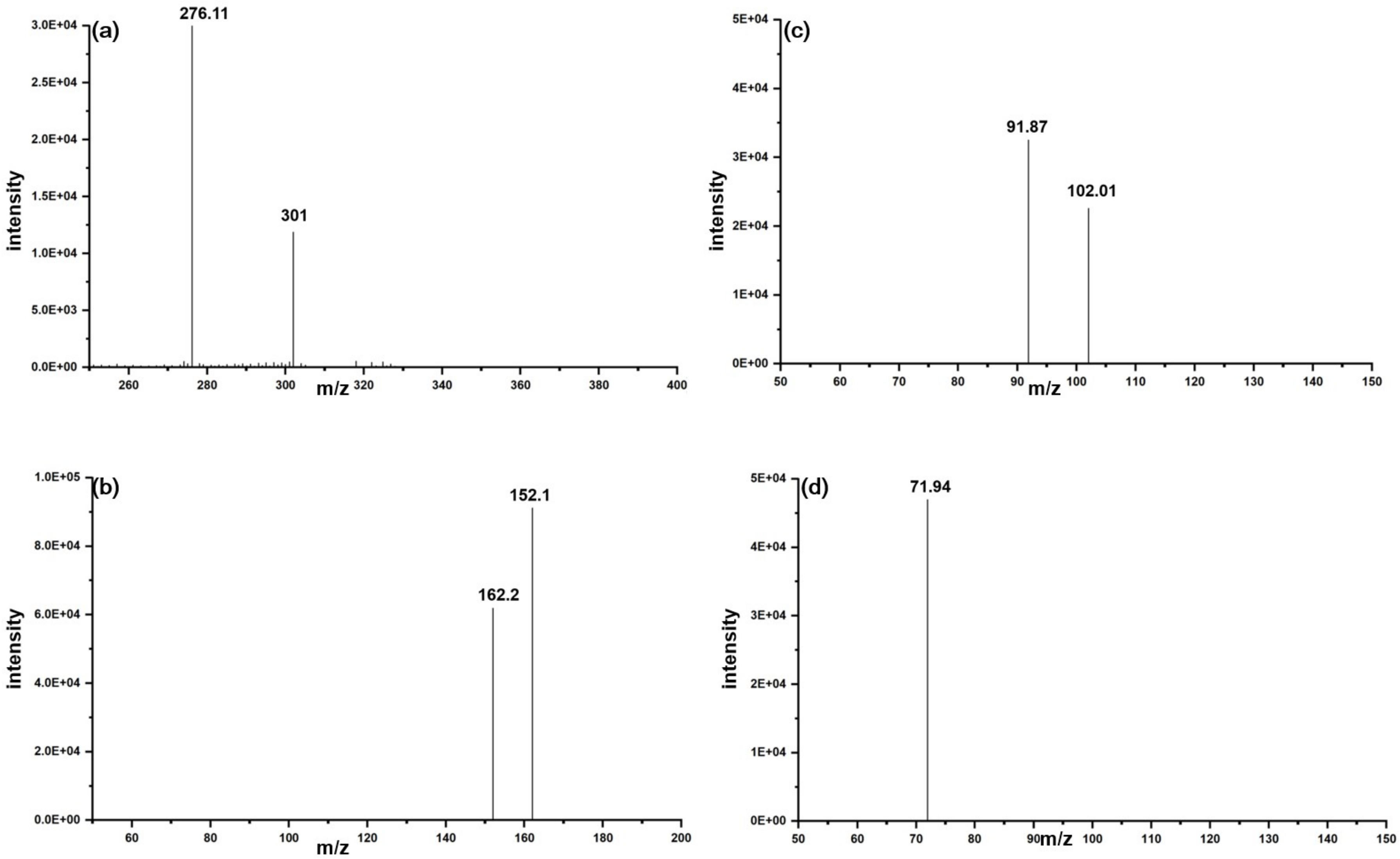


(a)
[M+H]+ 127
2,2-Dichloroacetamide
intensity
m/z
(b)
207 [M+H]+
[M-H]- 205
2-bromo-5-chlorophenol
intensity
m/z
(c)
389 [M+H]+
3,5diiodosalicylic acid
intensity
m/z
(d)
[M-H]- 232
234
[M+H]+
Diuron
intensity
m/z



(e)
[M+H] + 262
Flumequine
intensity
m/z
(g)
[M+H] +320
Norfloxacin
intensity
m/z
(f)
[M-H] - 248
250 [M+H] +
Linuron
intensity
m/z

Figure S4. Mass spectra of 2,2-Dichloroacetamide (1000 µg/L) (a), 2-Bromo-5-chlorophenol (1000 µg/L) (b), 3,5-diiodasalicylic acid (1000 µg/L) (c), diuron (1000 µg/L) (d), flumequine (1000 µg/L) (e), linuron (1000 µg/L) (f), norfloxacin (1000 µg/L) (g) from soft microwave plasma torch mass spectrometer with power of 115 W and a microwave frequency of 2.45 GHz.


(a)
276.11
301
intensity
m/z
(b)
152.1
162.2
intensity
m/z
(c)
91.87
102.01
intensity
m/z
(d)
71.94
intensity
m/z

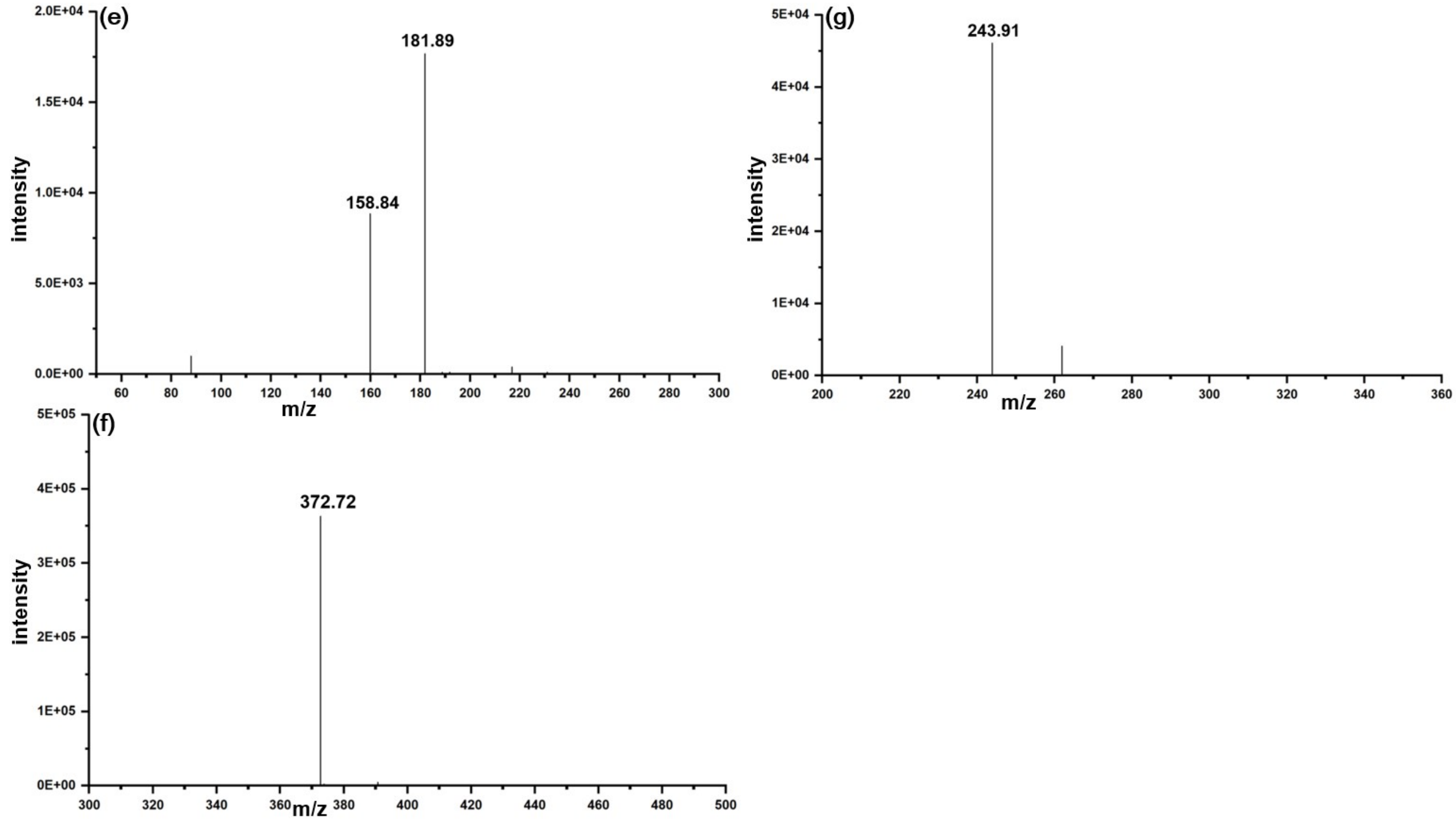
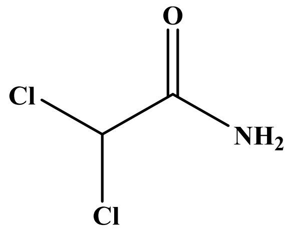
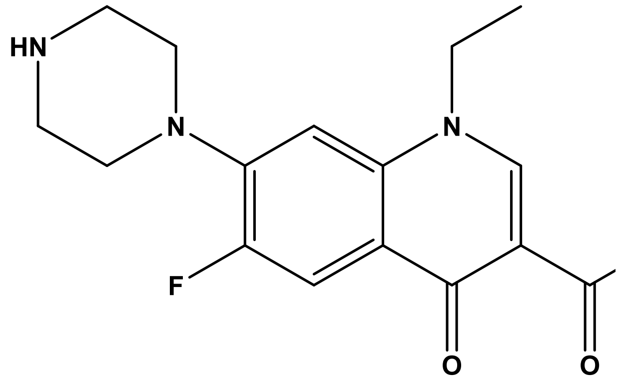
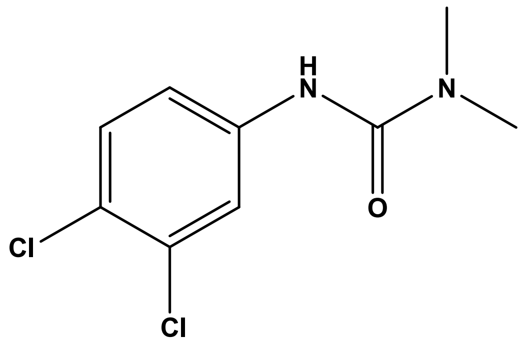
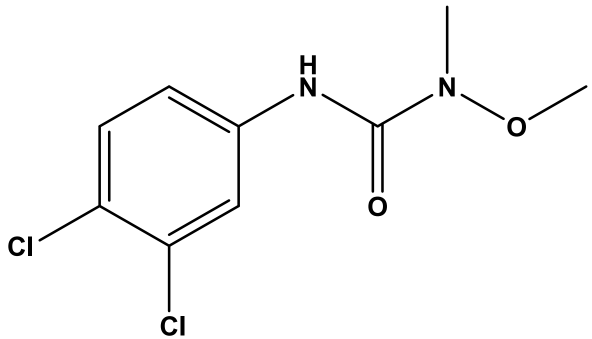
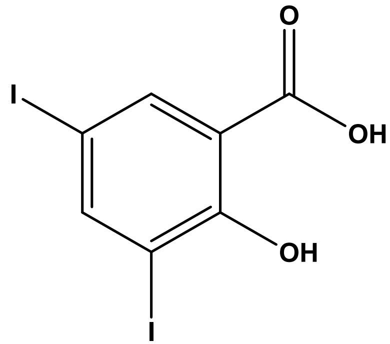
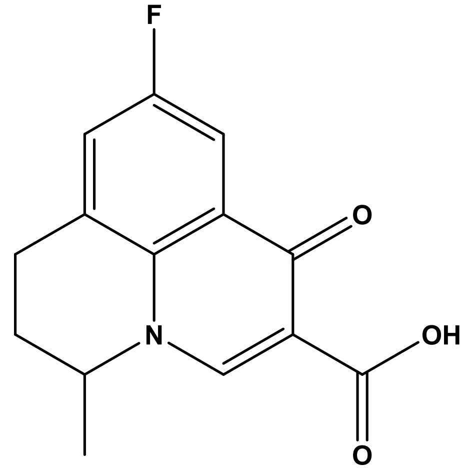
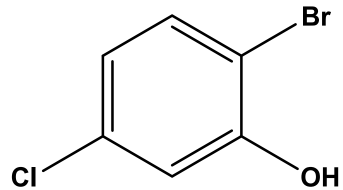


Figure S5. MS/MS Spectra of norfloxacin (m/z 320) (a), 2-Bromo-5-chlorophenol (m/z 207) (b), 2,2-Dichloroacetamide (m/z 127) (c), diuron (m/z 232) (d), linuron (m/z 248) (e), 3,5-diiodasalicylic acid (m/z 389) (f), flumequine (m/z 262) (g)

Table S1 Basic physicochemical properties of H-compounds.

H- compounds	Molecular formula	Molecular weight (m/z)	Ion form	MS^2	Molecular structure
2,2,-dichloroacetamide	$C_2H_3Cl_2N$	126	127 $[M+H]^+$	91.87/102	
Norfloxacin	$C_{16}H_{18}FN_3$	319	320 $[M+H]^+$	276.11/301	
Diuron	$C_9H_{10}Cl_2N_2O$	233	232/234 $[M+H]^+$ and [M+H]-	71.90	

Linuron	$C_9H_{10}Cl_2N_2O_2$	249	248/250 $[M+H]^+$ and [M+H]-	158.84/181.89	
3,5diiodasalicylic acid	$C_7H_4I_2O_3$	389.82	39 $[M+H]^+$	372.72	

Flumequine	**$C_{14}H_{12}FNO_3$**	261	262 [M+H]$^+$	243.91	
2-Bromo-5-chlorophenol	**C_6H_4BrClO**	207.45	205/207 [M+H]$^+$ and [M+H]-	162.2/152.1	

The coefficient of variation (CV) and the Standard deviation (Std Dev) measure relative variability are essential in assessing the precision of the recovery percentages. Some compounds show lower CV values, indicating more consistent recovery across samples from flooding irrigation systems. The p-values suggest that there are no significant differences between the groups' mean recovery percentages at a typical alpha level of 0.05. This means we cannot reject the null hypothesis that the means are equal.

However, from sub-irrigation systems, the variability, especially in 2-bromo-5-chlorophenol, highlighted by the higher CV, suggests that specific compounds may experience different interactions within the system.

The CV values from the lateral move irrigation system indicate that 3,5-diiodasalicylic acid shows the highest variability among the detected compounds, suggesting more fluctuations in its recovery rates across samples. Others exhibit lower CVs, indicating more consistent recovery rates.

This comprehensive statistical analysis helps validate the consistency of the detection method, supporting its reliability for analyzing these compounds in water samples.

Table S2 Statistical data for consistency validation of detection method.

Samples	Compounds	Std Dev	CV	Samples	Std Dev	CV	Samples	Std Dev	CV
Flood irrigation system	**2,2,-dichroloacetamide**	8.21	8.69	Lateral move irrigation system	7.29	8.00	Sub-irrigation systems	8.77	9.41
	Diuron	6.54	5.86		7.35	6.71		7.96	8.31
	Flumequine	5.78	5.01		8.51	7.54		8.03	6.79
	2-bromo-5-chlorophenol	5.83	5.25		6.89	8.01		10.33	11.56
	Norfloxacin	8.19	7.84		8.18	7.71		9.08	8.05
	Linuron	9.97	8.91		7.99	9.02		9.31	9.07
	3,5diiodasalicylic acid	7.86	8.01		8.55	12.57		8.70	8.24

Table S3 Statistical data for consistency validation of detection method.

Samples	Compounds	Std Dev	CV	Samples	Std Dev	CV	Samples	Std Dev	CV
Flood irrigation system	Zinc	7.04	7.29	Lateral move irrigation system	5.81	5.17	Sub-irrigation systems	5.22	5.55
	Manganese	4.44	8.11		7.15	7.01		6.76	5.81
	Nickel	7.08	6.53		6.90	7.04		6.13	5.92
	Lead	5.68	6.55		8.01	6.98		6.33	5.56

CV: Coefficient of Variation, Std Dev: Standard deviation

ANOVA p-value: Flood irrigation system = 0.4105, Lateral move irrigation system = 0.4071, Sub-irrigation systems = 0.4094