Supporting Information

Development of a fully automatic separation system coupled with online ICP-MS for measuring rare earth elements in seawater

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Section. Calibration methods

A NexION^{TM} 350D ICP-MS (PerkinElmer, USA) was used for the determination of REEs in this study. For this study, the standard mode of the ICP-MS was used for the determination of ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{153}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{172}Yb and ^{175}Lu. Calibration curves were constructed using mixed REE standard solutions (0.5, 1, 2, 5, 10 and 20 ng L^{-1}) and linear correlation coefficients ($R^2 > 0.999$) were calculated for all REEs. The accuracy (the relative standard deviation, RSD) of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu elements are 0.17%, 0.09%, 0.16%, 0.11%, 0.36%, 0.37%, 0.52%, 0.91%, 0.03%, 0.29%, 0.41%, 1.39%, 0.64% and 1.06%, respectively. The eluent with the target elements was injected into the spray chamber of the ICP-MS through a concentric glass nebulizer and quartz ball joint injector. Rhodium (Rh) was added to all samples and standards at a concentration of 100 μg L^{-1} to check the elution proceeded properly.

Fig. S1 Effect of the sample injection volume on the signal intensity (A), the ratio of signal to background (B), and the relative standard deviation (C). A mixed REEs standard solution (10 ng L^{-1} for each element) was used in this experiment.

Fig. S2 Sampling sites from the Pearl River Estuary (Guangdong, China) between 9th to 11th July, 2021.

Table S1 The salt (%), pH value, and conductivity of 18 collected water samples

Table S2 REEs concentrations of river and seawater samples (ng L^{-1})

Table S3 REEs patten (PAAS Normalized values) and Gd_N/Gd_N^* of river and seawater samples

Fig. S3 Scatter diagrams of salt (A) and PH (B) vs ∑REE diagram for all seawaters.

Table S4 Comparison of the ELSPE-2 Precon system, SeaFASTTM system and CETAC DSX-100 system

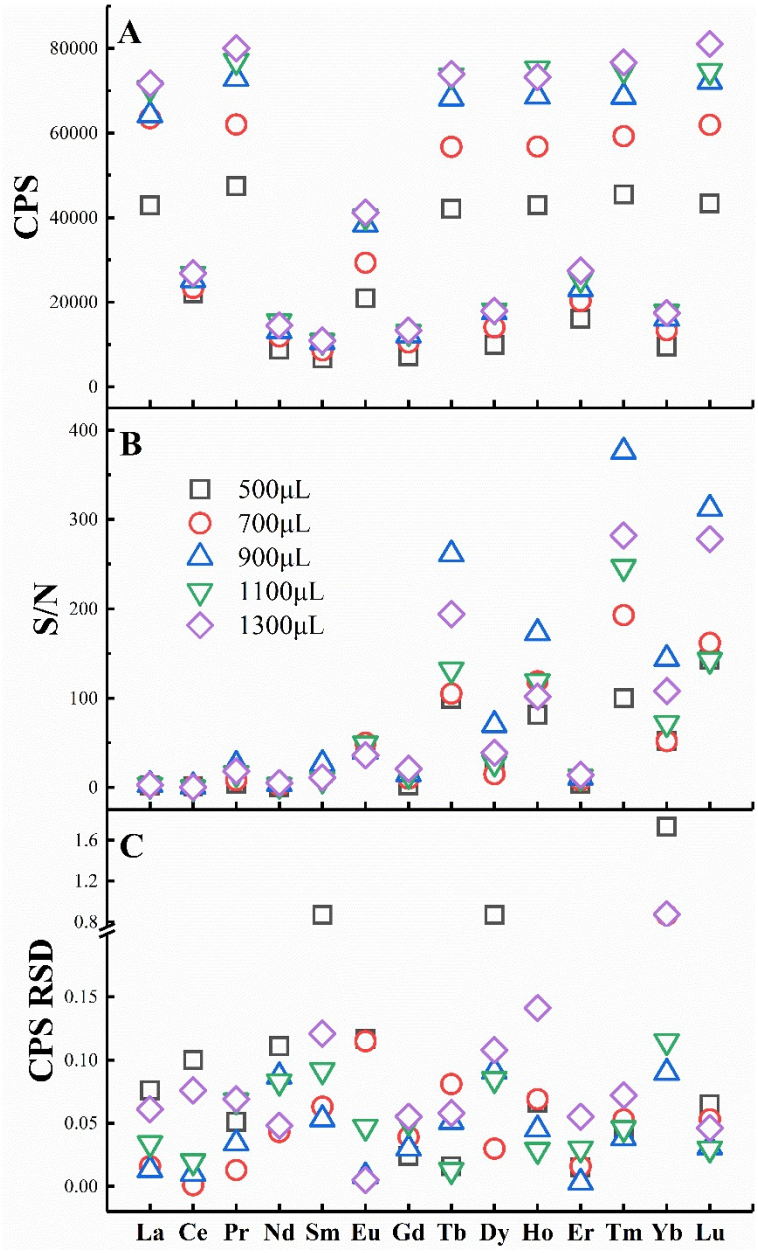

Fig. S1 Effect of the sample injection volume on the signal intensity (A), the ratio of signal to background (B), and the relative standard deviation (n=3) (C). A mixed REEs standard solution (10 ng L^{-1} for each element) was used in this experiment.

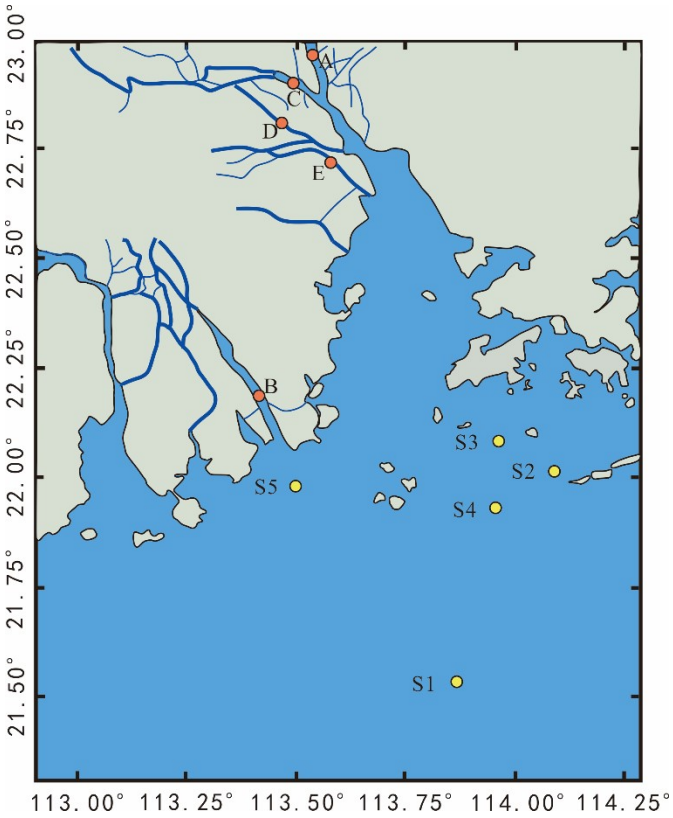

Fig. S2 Sampling sites from the Pearl River Estuary (Guangdong, China) between 9th to 11th July, 2021.

Table S1 The salt (%), pH value, and conductivity of 18 collected water samples

Sample	Descriptions	Salt (%)	pH value	Conductivity (ms/cm)
S1 SS	Surface seawater	3.21	8.16	52.4
S1 IW	Intermediate seawater	3.26	8.11	52.5
S1 BS	Bottom seawater	3.30	7.96	53.1
S2 SS	Surface seawater	2.91	7.93	47.5
S2 IW	Intermediate seawater	3.20	8.02	52.7
S2 BS	Bottom seawater	3.19	7.91	52.5
S3 SS	Surface seawater	2.50	8.02	42.0
S3 IW	Intermediate seawater	3.01	7.89	49.6
S3 BS	Bottom seawater	0.85	7.74	19.0
S4 SS	Surface seawater	2.59	8.26	44.5
S4 IW	Intermediate seawater	3.20	7.96	52.8
S4 BS	Bottom seawater	3.19	7.88	52.5
S5 SS	Surface seawater	1.03	7.60	21.8
A RW	River water	<0.2	8.01	6.2
B RW	River water	<0.2	7.84	0.8
C RW	River water	<0.2	7.73	0.8
D RW	River water	<0.2	8.10	0.3
E RW	River water	<0.2	7.86	0.3

Table S2 REEs concentrations of river and seawater samples (ng L^{-1})

REEs	A RW	B RW	C RW	D RW	E RW	S1 SS	S1 IW	S1 BS	S2 SS	S2 IW	S2 BS	S3 SS	S3 IW	S3 BS	S4 SS	S4 IW	S4 BS	S5 SS
La	3.29	3.17	2.30	14.33	8.57	5.28	4.58	1.22	0.48	2.45	1.38	0.31	0.92	1.48	7.44	6.38	5.03	4.94
Ce	1.32	1.63	2.01	12.79	6.26	3.99	4.00	2.61	0.88	3.25	1.87	0.06	0.36	2.21	5.45	4.20	3.20	4.61
Pr	0.82	1.20	1.25	3.59	2.25	1.37	1.30	0.69	0.55	1.16	0.87	0.23	0.06	1.04	2.30	2.06	1.21	2.39
Nd	3.11	4.16	3.36	14.47	8.84	3.21	5.87	3.22	3.27	4.99	3.88	0.97	0.76	4.57	9.01	7.14	5.02	9.35
Sm	0.88	0.93	1.96	3.69	2.41	1.11	1.30	1.63	1.62	2.29	0.88	0.99	0.41	0.87	2.94	2.26	1.74	1.93
Eu	0.65	0.67	1.41	0.95	0.69	0.36	0.41	0.33	0.34	0.30	0.43	0.57	0.25	0.22	0.64	0.77	0.61	0.77
Gd	7.77	2.76	2.61	6.14	3.43	2.22	2.67	1.34	2.94	2.21	1.25	2.07	1.77	2.11	3.53	3.03	1.56	3.12
Tb	0.21	0.22	0.71	0.72	0.38	0.26	0.41	0.21	0.25	0.31	0.36	0.77	0.42	0.35	0.63	0.92	0.70	0.62
Dy	1.24	1.03	1.92	4.36	2.29	1.97	2.32	1.38	3.03	2.03	2.21	3.06	3.03	2.86	4.03	2.70	2.57	2.75
Ho	0.46	0.47	0.73	0.64	0.55	0.66	0.54	0.41	0.87	0.51	0.51	1.31	0.88	0.84	0.90	1.14	0.91	0.96
Er	3.05	1.86	2.36	4.43	2.95	1.71	2.93	1.04	2.70	2.23	1.55	3.06	2.99	4.31	3.92	3.67	2.10	2.95
Tm	0.79	0.35	1.09	0.67	0.41	0.24	0.23	0.19	0.42	0.31	0.33	0.65	0.36	0.33	0.45	0.79	0.51	0.64
Yb	6.84	3.35	2.77	4.05	2.84	1.96	1.85	1.05	2.16	1.90	1.48	3.50	2.32	2.67	3.44	2.80	2.33	2.73
Lu	1.36	0.51	1.41	0.79	0.51	0.24	0.27	0.08	0.31	0.23	0.20	0.67	0.44	0.33	0.34	0.51	0.42	0.60
∑REE	31.8	22.3	25.9	71.6	42.4	24.6	28.7	15.4	19.8	24.2	17.2	18.2	15.0	24.2	45.	38.4	27.9	38.4

RW: River Water;

SS: Surface seawater;

IW: Intermediate seawater;

BS: Bottom seawater;

∑REE= Total REE concentrations

Table S3 REEs patten (PAAS Normalized values) and Gd_N/Gd_N^* of river and seawater Samples

REEs	A RW	B RW	C RW	D RW	E RW	S1 SS	S1 IW	S1 BS	S2 SS	S2 IW	S2 BS	S3 SS	S3 IW	S3 BS	S4 SS	S4 IW	S4 BS	S5 SS
La	0.07	0.07	0.05	0.32	0.19	0.12	0.10	0.03	0.01	0.05	0.03	0.01	0.02	0.03	0.17	0.14	0.11	0.11
Ce	0.01	0.02	0.02	0.14	0.07	0.05	0.05	0.03	0.01	0.04	0.02	0.00	0.00	0.03	0.06	0.05	0.04	0.05
Pr	0.08	0.12	0.12	0.35	0.22	0.14	0.13	0.07	0.05	0.11	0.09	0.02	0.01	0.10	0.23	0.20	0.12	0.24
Nd	0.08	0.11	0.09	0.39	0.24	0.09	0.16	0.09	0.09	0.13	0.10	0.03	0.02	0.12	0.24	0.19	0.13	0.25
Sm	0.13	0.13	0.28	0.54	0.35	0.16	0.19	0.24	0.24	0.33	0.13	0.14	0.06	0.13	0.43	0.33	0.25	0.28
Eu	0.54	0.55	1.16	0.79	0.56	0.29	0.34	0.28	0.28	0.25	0.35	0.47	0.20	0.18	0.53	0.63	0.50	0.64
Gd	1.29	0.46	0.43	1.02	0.57	0.37	0.44	0.22	0.49	0.37	0.21	0.34	0.29	0.35	0.58	0.50	0.26	0.52
Tb	0.24	0.25	0.80	0.81	0.42	0.29	0.46	0.24	0.28	0.34	0.40	0.87	0.47	0.39	0.71	1.03	0.78	0.70
Dy	0.23	0.19	0.36	0.82	0.43	0.37	0.44	0.26	0.57	0.38	0.41	0.58	0.57	0.54	0.76	0.51	0.48	0.52
Ho	0.44	0.44	0.69	0.61	0.52	0.63	0.51	0.39	0.82	0.48	0.49	1.24	0.84	0.80	0.86	1.09	0.87	0.91
Er	0.99	0.60	0.77	1.44	0.96	0.56	0.95	0.34	0.88	0.72	0.50	1.00	0.97	1.40	1.27	1.19	0.68	0.96
Tm	1.75	0.78	2.41	1.48	0.91	0.52	0.50	0.43	0.94	0.70	0.74	1.44	0.80	0.73	0.99	1.75	1.13	1.43
Yb	2.27	1.11	0.92	1.35	0.94	0.65	0.61	0.35	0.72	0.63	0.49	1.16	0.77	0.89	1.14	0.93	0.78	0.91
Lu	3.10	1.16	3.22	1.81	1.17	0.55	0.61	0.17	0.70	0.53	0.47	1.52	1.00	0.76	0.78	1.17	0.96	1.36
$LREE_N/MREE_N$	0.40	0.52	0.18	0.49	0.54	0.41	0.36	0.25	0.14	0.29	0.23	0.03	0.04	0.24	0.34	0.29	0.24	0.40
$HREE_N/MREE_N$	11.9	5.31	4.54	2.14	2.52	2.09	1.60	1.29	2.18	1.75	1.80	2.60	2.34	2.25	1.54	2.06	1.89	2.47
Gd_N/Gd_N^*	6.44	2.17	0.69	1.41	1.42	1.48	1.20	0.93	1.85	1.08	0.67	0.54	0.88	1.15	0.95	0.63	0.42	0.92

RW: River Water; SS: Surface seawater; IW: Intermediate seawater; BS: Bottom seawater.

$LREE_N=La_N+Pr_N+Nd_N$; $MREE_N=Sm_N+Tb_N+Dy_N$; $HREE_N=Tm_N+Yb_N+Lu_N$;

$Gd_N/Gd^*_N=Gd_N/(0.33\ Sm_N+0.67\ Tb_N)$;

where the subscript N denotes normalization to PAAS and the superscript * represents the geogenic background.

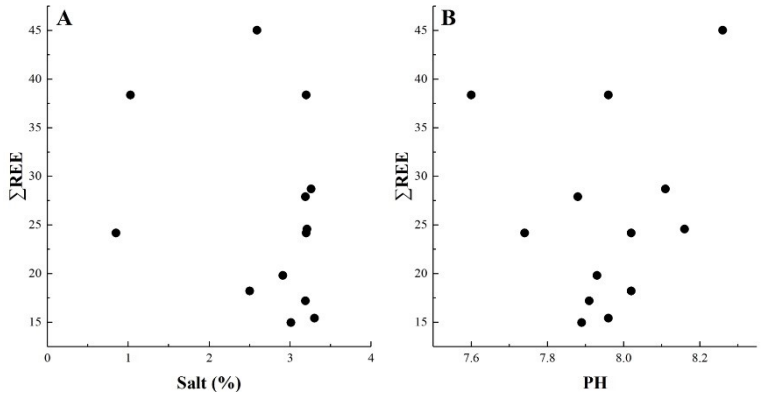

Fig. S3 Scatter diagrams of salt (A) and PH (B) vs ∑REE diagram for all seawaters.

Table S4 Comparison of the ELSPE-2 Precon system, SeaFASTTM system and CETAC DSX-100 system

	ELSPE-2 Precon system	SeaFAST^{TM} system	CETAC DSX-100 system
Particle size (μm)	5 μm	75 μm	0.2 μm
Analysis efficiency	~ 4 min/sample	~ 9 min/sample (Inline)/ ~ 15 min/sample (Offline)	1 h/sample
Sample consumption	＜1 mL	7~11 mL	120 mL
Volume	0.5*0.5*0.4 m	1.5*1*0.6 m	--
Cost	< $ 50 000	＞ $ 100 000	--

"--" means no data; The data about SeaFAST^{TM} system are obtained from the website (https://www.icpms.com/products/sea-fast.php) and the literatures (Hathorne et al., 2012; Behrens et al., 2016); The data about CETAC DSX-100 system are come from the literature (Kühn et al., 2000).

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