



Supplement of

Measurement of soluble aerosol trace elements: inter-laboratory comparison of eight leaching protocols

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1 **Table S1.** Summary of the leaching protocol used at GIG (Zhang et al., 2022).

Batch/Flow through	Batch
Leach medium	Ultrapure water
Volume	20 mL
pH	6.5
Agitation	Continuous agitation by orbital shaker (300 r/min) for 2 h at room temperature.
Filter pore size	0.22 μm
Storage prior to analysis	Filters stored frozen.
Method steps	1) Place the shredded filter in an acid-cleaned 20 mL Corning tube. 2) Add 20 mL of ultra-high purity water. 3) Cap the tube and stir it by an orbital shaker (300 r/min) for 2 h. 4) Filter the extraction into another acid-cleaned 20 mL Corning tub. 5) Acidify the solution to contain 1% HNO_3 , and cap the tube. 6) Store the leachate refrigerated until analysis by Q-ICP-MS.

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6 **Table S2.** Summary of the leaching protocol used at NIO (Panda et al., 2022).

Batch/Flow through	Batch
Leach medium	Ultrapure water
Volume (mL)	20
pH	6.4
Agitation (Y/N, type, time/speed/temp)	Y, Ultrasonication, 30 min (in 2 cycles of 15 min for each, to maintain the room temperature), 25°C
Filter pore size	0.2 µm
Storage prior to analysis	Filters stored frozen.
Method steps	1) Place the shredded filter in a pre-cleaned 50mL Savillex PFA vials. 2) Add 20 mL of ultrapure water into the vial. 3) Cap the vial and keep it in an ultrasonicator for 30 minutes agitation (but in 2 cycles of 15 min each, to maintain room temperature). 4) Prepare a non-metallic syringe with a plastic plunger to be used for filtration. The syringe is fitted with a 0.2 µm PVDF filter rinsed 3 times with ultrapure water. 5) Rinse the PVDF filter and syringe with 2-3 mL leachate (this aliquot is discarded), and then filter the remaining leachate into a pre-cleaned polypropylene bottle. 6) Acidify the filtered leachate with 1-2 drops of Suprapure HNO₃, and cap the bottle. 7) Store the leachate in a refrigerator at 4°C until analysis by HR-ICP-MS.

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11 **Table S3.** Summary of the leaching protocol used at UEA (Sarhou et al., 2003).

Batch/Flow through	Batch
Leach medium	Ammonium acetate (1.1 mol/L)
Volume	20 mL
pH	4.7
Agitation	Gentle agitation by hand every 5 min for 1 h at room temperature.
Filter pore size	0.2 µm
Storage prior to analysis	Filters stored frozen.
Method steps	1) Place the filter in an acid-cleaned 50 mL Corning tube. 2) Add 20 mL of ultra-high purity ammonium acetate solution (pH = 4.7). 3) Cap the tube and agitate it gently by hand for 1 min. 4) Repeat Step 3 every 5 min for 1 h. 5) Rinse the syringe filter with 10 mL UHP water and discard the solution. 6) Rinse the syringe filter with 4-5 mL of sample and discard the solution. 7) Filter the remaining sample into a suitable acid-cleaned Corning tube and cap the tube. 8) Store the leachate refrigerated at 4 °C until analysis by TQ-ICP-MS and ICP-OES.

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Table S4. Summary of the leaching protocol used at UGA (Buck et al., 2013).

Batch/Flow through	Leach 1 (soluble): flow through	Leach 2: batch leaching
Leach medium	Ultrapure water	25% acetic acid (v/v) + 0.02 mol/L hydroxylamine hydrochloride
Volume (mL)	100	10
pH	5.6	2
Agitation	No agitation	No agitation
Filter pore size	0.2 μ m	No backing filter
Storage prior to analysis	Frozen	
Method steps	Leach 1: flow through 1) Mount the sample filter into the filter holder along with a 0.2 μm backing filter. 2) Place the labeled receiving bottle inside the vacuum chamber. 3) Carefully pour 100 mL of ultrapure water onto the filter. 4) Keep the filter covered evenly with water (exposure time: ~20 s). 5) Switch off the pump when all water has passed through the filter and into the bottle 6) Remove the bottle from the chamber and acidify the solution to 0.024 mol/L HCl. 7) Store the leachate frozen for until analysis by Q-ICP-MS. Leach 2: batch leaching 1) Fold the filter in half (particles inward), and then in half again; fold it twice more to give a small rectangle. Use the tweezers to press down and make the folded filter as compact as possible. 2) Place the folded filter into a 15 mL acid-washed centrifuge tube. 3) Add 5 mL of leach solution (25% acetic acid (v/v) + 0.02 mol/L hydroxylamine hydrochloride) with Rh spike. 4) Heat the tube in a water bath to 90-95 °C for 10 min. 5) Remove the tube from the water bath and allow it to cool for 110 min. 6) Centrifuge the tube for 5 min at 4500 rpm and decant the supernatant to a Savillex perfluoroalkoxy (PFA) vial. 7) Add 2.5 mL of ultrahigh purity water to the centrifuge tube and repeat centrifugation. Decant the supernatant. 8) Repeat step 7. 9) Pipette 100 μL of concentrated double-distilled HNO₃ to the PFA vial 10) Dry down the PFA vial contents, and then add 5 mL of 2% Optima HNO₃ (v/v). Cap the vial and heat it at 140 °C for 30 minutes. 11) Allow the vial to cool, and then transfer the solution in the vial to a storage bottle until analysis.	

20 **Table S5.** Summary of the leaching protocol used at UoP (Buck et al., 2010).

Batch/Flow through	Flow Through
Leach medium	Ultrapure water
Volume	100 mL
pH	5.2
Agitation	No agitation
Filter pore size	0.2 µm
Storage prior to analysis	Filters stored frozen at -20 °C until processing.
Method steps	1) A pre-washed 0.2 µm polycarbonate backing filter was placed on the acid-clean perfluoroalkoxy alkanes Savillex filtration assembly, using tweezers. 2) An aerosol filter was loaded onto backing filter and opened with tweezers. 3) The receiving chamber was secured on top of the filtration assembly 4) Vacuum pump was turned on, and 100 mL ultra-high purity water was passed over the filter via the receiving chamber (flow rate: ~240 ml/min). 5) Vacuum was maintained for 45 seconds to ensure that the filter was dry. 6) The leachate was decanted into a 125 mL acid-clean low density polyethylene bottle. 7) The leachate was acidified to 0.3 mol/L HNO₃ (2% v/v). 8) Multi-element analysis by iCAP TQ ICP-MS.

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Table S6. Summary of the leaching protocol used at UTAS (Perron et al., 2020).

Batch/Flow through	Leach 1 (soluble): flow through	Leach 2: batch leaching
Leach medium	ultrapure water	ammonium acetate (1.1 mol/L)
Volume (mL)	50 mL	10 mL
pH	6.5	4.7
Agitation	No agitation	Gentle hand shaking every 15 min during the 1-h batch leach.
Filter pore size	no backing filter	no backing filter
Storage prior to analysis	Filters stored frozen (-20 °C) until processing in the lab.	
Method steps (sequential leaches)	Leach 1: flow-through 1) Place the filter (using tweezers) in an acid-cleaned Savillex filter holder mounted on top of a Teflon filtration (vacuum) chamber. 2) Pour 50 mL of ultrapure water through the top column placed on top of the filter holder and switch the pump on until the filter is dry again (2-3 min) 3) Pipette 9.7 mL of the leachate in a clean PP tube, add 0.2 mL of ultra-high purity HNO₃ and 0.1 mL of 1 ppm In internal standard. The soluble fraction is analyzed by SF-ICP-MS on the next day. Leach 2: batch leaching 4) Place the leached filter in a centrifuge tube. 5) Pour 10 mL of freshly made ammonium acetate solution (pH = 4.7) in the tube (submerged filter). 6) Leave the ammonium acetate batch solution to react for 60 min while hand-shaking the tube roughly every 15 min. 7) At 45 min time, place the tube in a centrifuge for 3 min at 4200 rpm so that the filter rests at the bottom of the tube. 8) Pipette 4.5mL of the ammonium acetate leachate in a Teflon vial (the filter stays in the tube) and evaporate the solution on a hotplate at 120 °C until dryness. 9) Add 4.45 mL of 2% v/v HNO₃ to the vial and reflux (Teflon vial lid closed) at 120 °C on a hotplate for 2-3 h to homogenize the solution. 10) Pour the solution in a PP tube and add 0.05 mL of 1 ppm In internal standard. The leachate is analyzed by SF-ICP-MS within 2-3 days. The labile fraction of trace elements is provided by the sum of their contents in the ultrapure water and ammonium acetate leaches.	

Table S7. Analytical methods used by each of the six groups to determine trace elements. Standards were aqueous solutions used to produce calibration curves, and reference materials were aqueous solutions used to check instrument analysis accuracy.

Group	Instrumentation	Standards	Reference materials
GIG	ICP-MS, iCAP Q	Multi-elemental standard (National Analysis and Testing Center for Nonferrous Metals and Electronic Materials, China)	NIST 1643f
NIO	HR-ICP-MS (Nu-ATTOM-ES)	Inorganic Ventures ICP standard 71A	Instead of using aqueous solutions, NIO used solid phase materials (Arizona test dust and NIST-SRM-2710a) to check their digestion recovery and analysis accuracy.
UEA	ICP-OES, i-CAP; ICP-MS, iCAP TQ	SPEX Certiprep individual standards	TM27.3, TMDA62.3, TMDA64.3 (Environment Canada)
UGA	Perkin Elmer Nexion 300D ICP-MS	Inorganic Ventures ICP standard 71A	NIST 1643f
UoP	ICP-MS, iCAP TQ	LabKings multi-elemental standard	Certified Standards (SCP™, ROMIL™)
UTAS	SF-ICP-MS, Element 2 (Thermo Fisher Scientific)	Multi-elemental solutions Municipal/Industrial Strategy for Abatement (MISA)-1, MISA-5 and MISA-6	NIST 1640a

35 **Table S8.** Summary of analytical detection limits (ng) reported for each method used by participating groups. Please note that different groups
36 may use different definitions of analytical blanks to calculate their detection limits. UGA and UTAS used sequential leaching protocols, and
37 reported analytical detection limits for the soluble fraction (UGA-u, UTAS-u) and for the sum of the first and second leaches (UGA-b, UTAS-a).
38 *: Elevated Ni blank due to the use of clean unexposed (new) Ni cones in the SF-ICP-MS instrument.

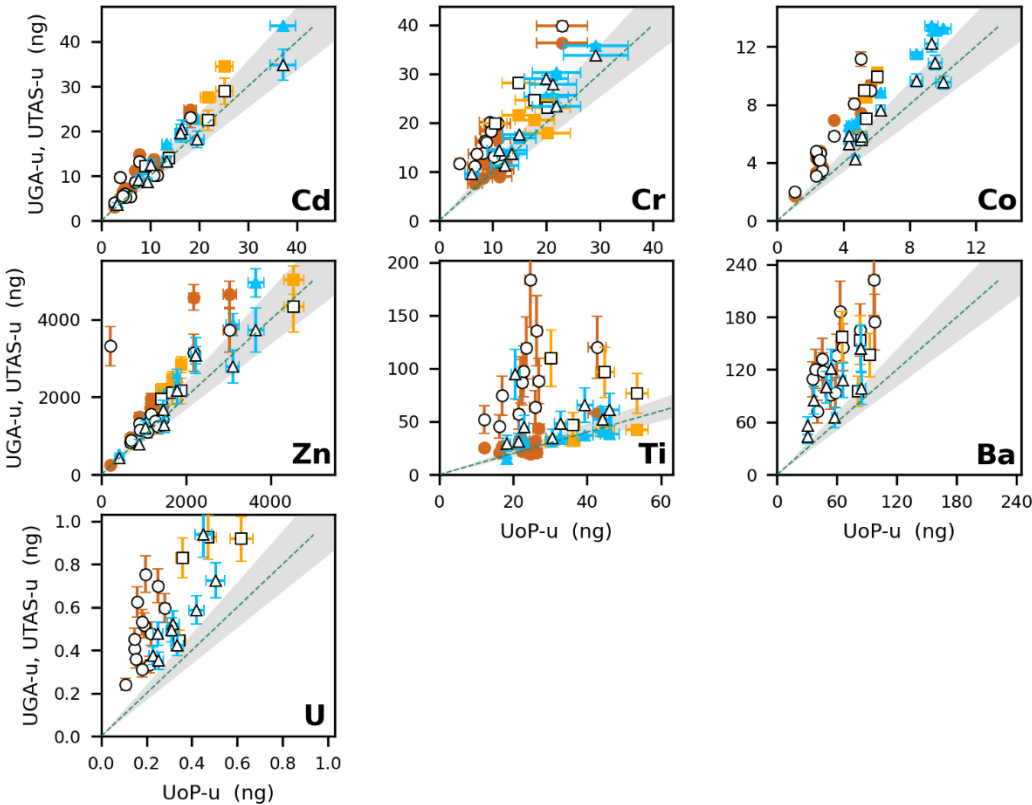
Trace element	GIG-u	NIO-u	UEA-a	UGA-u	UGA-b	UoP-u	UTAS-u	UTAS-a
Al	34	1.9	6.4	17	21	5.7	6	6.1
As	4		0.4					
Ba	36		1.2			0.06	0.77	0.79
Cd	1		0.2	1.56	1.5	0.029	0.17	0.17
Ce			0.2				0.096	0.097
Co		0.1	0.1	0.55	0.57	0.0075	0.069	0.07
Cr	10		0.7	7.4	7.9	0.29	0.14	0.15
Cu	14	0.19	2.7	24	74	0.13	0.27	0.3
Fe	16	18	5	39	42	0.41	1.2	1.3
La			0.3				0.11	0.11
Mn	20	0.94	1.4	7.9	8.1	0.18	0.076	0.079
Ni	6	11	2	5	5.2	0.21	23*	23*
P		3.8	8.2				1.7	2
Pb	4	1.7	0.2	2.5	2.6	0.0067	0.33	0.34
Sb	10		0.1					

Th		0.11	0.5				0.3	0.3
Ti		5.8	0.6	15	16	0.053	0.26	0.26
U			0.1			0.0014	0.096	0.098
V	2	0.017	0.6	5.8	5.8	0.0075	0.12	0.12
Zn	36		2.6	28	28	1.4	3.3	3.4

Table S9. Blank values, BCDL (blank-correction detection limits) and B/IC (the ratio of the blank to the lowest mass measured in the D samples) for each of the trace elements determined for each method/group. Only trace elements for which the blanks were above the analytical detection limits are listed. For all other trace elements (and for UGA-u and for NIO-u analysis), the measured blanks were below the analytical detection limits and thus no blank subtraction was performed. (a: high B:IC due to the trace element mass in D samples below the analytical detection limit.)

method	trace element	Blank (ng)	BCDL (ng)	B/IC (%)
GIG-u	Zn	36	37	57
UEA-a	Fe	7.9	4.1	0.5
	Ti	8.3	8.5	11
	Zn	6.5	4.3	0.7
UGA-b	Cr	0.57	0.3	3.8
	Fe	16	13	0.3
	Ti	8	4.4	53 ^a
UoP-u	Cr	0.68	0.70	15
	Ti	0.81	0.88	6.2
	U	0.0029	0.0039	2.6
	V	0.040	0.078	0.5
	Zn	9.0	25	4.0
UTAS-u	Al	10	3.2	0.7
	Cd	0.29	0.46	7.3
	Co	0.082	0.092	3.9
	Cr	0.18	0.34	1.9
	Cu	0.46	0.43	0.4
	Fe	3.2	1.8	0.3
	Ni	43	9.8	180 ^a
	P	11	4.8	2.9
	Ti	0.81	0.94	2.7
	V	0.13	0.06	1.1
UTAS-a	Al	28	20	1.1

Ba	0.94	1.6	0.5
Cd	1.3	2.1	19
Co	0.1	0.06	2.5
Cr	0.49	0.36	3.5
Cu	1.2	0.8	0.6
Fe	11	7.3	0.6
Mn	0.27	0.11	0.1
Ni	48	11	155
P	19	7.2	2.7
Pb	0.45	0.84	0.3
Ti	4.6	8.3	9.9
V	0.16	0.06	0.8
Zn	13	8.1	1.5



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50 **Figure S1.** Comparison of the absolute mass of soluble trace elements (Cd, Cr, Co, Zn, Ti, Ba
51 and U) obtained using ultrapure water flow-through leaching methods (UoP, UTAS and UGA).
52 Plot details are as described in Figure 3. UGA data are represented by solid symbols, and UTAS
53 data are represented by open symbols. No Ba and U data were available for the UGA-u method.

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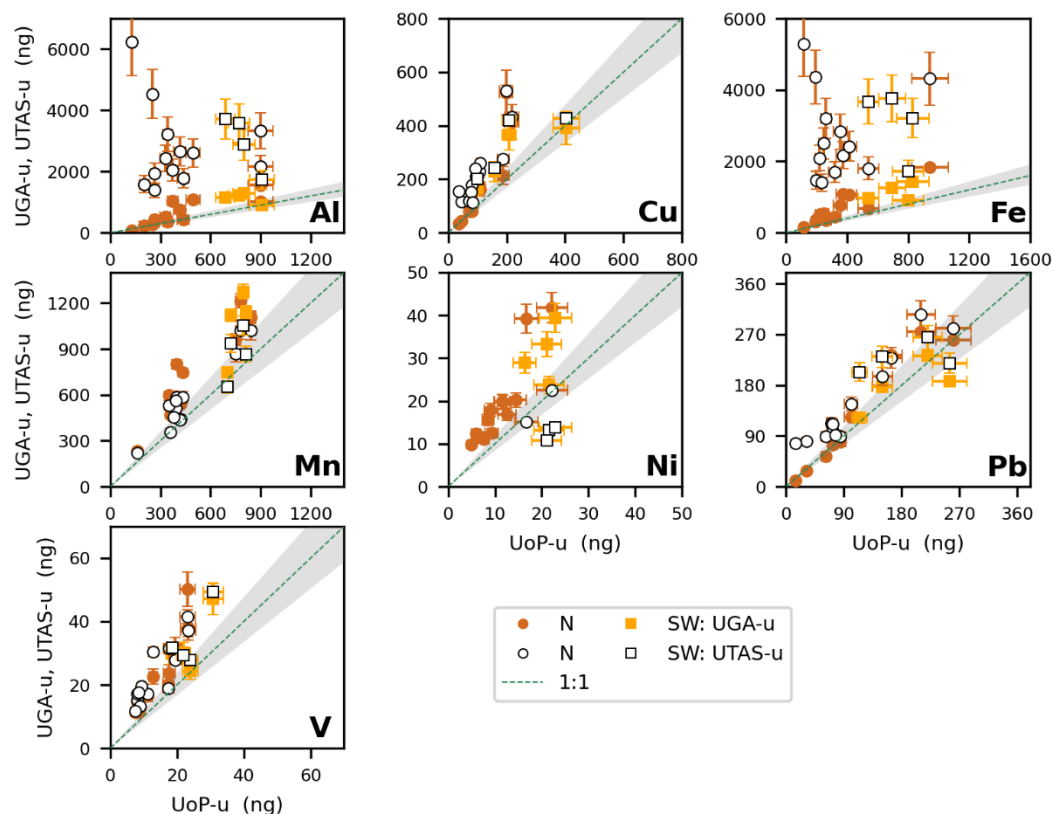


Figure S2. Comparison of the absolute mass of soluble trace elements obtained using ultrapure water flow-through leaching methods (UoP, UTAS and UGA). Plot details are as described in Figure 3. Compared to Figure 4, Figure S2 does not include data for YS samples. Values below detection limit are not plotted.

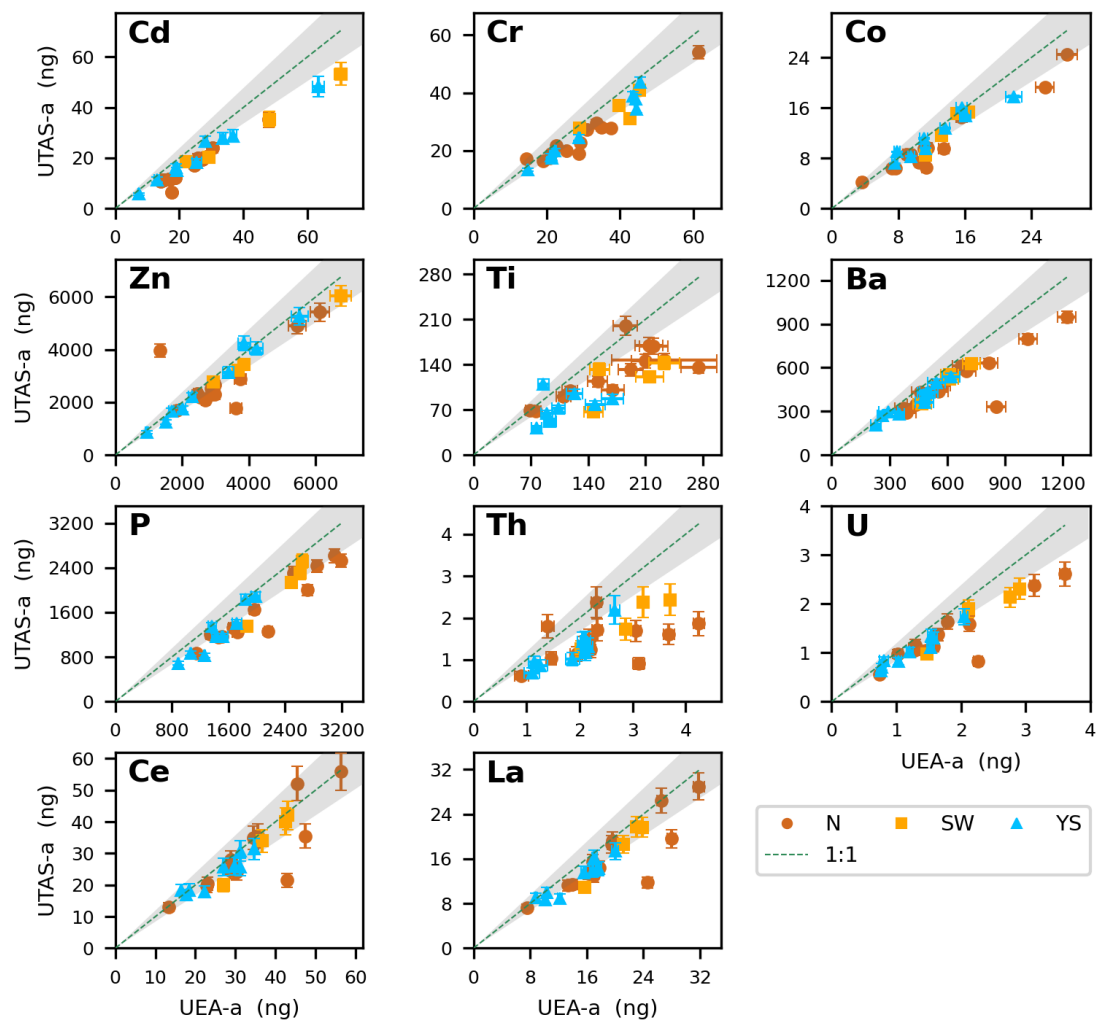


Figure S3. Comparison of the absolute mass of trace elements (Cd, Cr, Co, Zn, Ti, Ba, P, Th, U, Ce and La) obtained using ammonium acetate extraction methods (UEA and UTAS). Plot details are described in Figure 3.

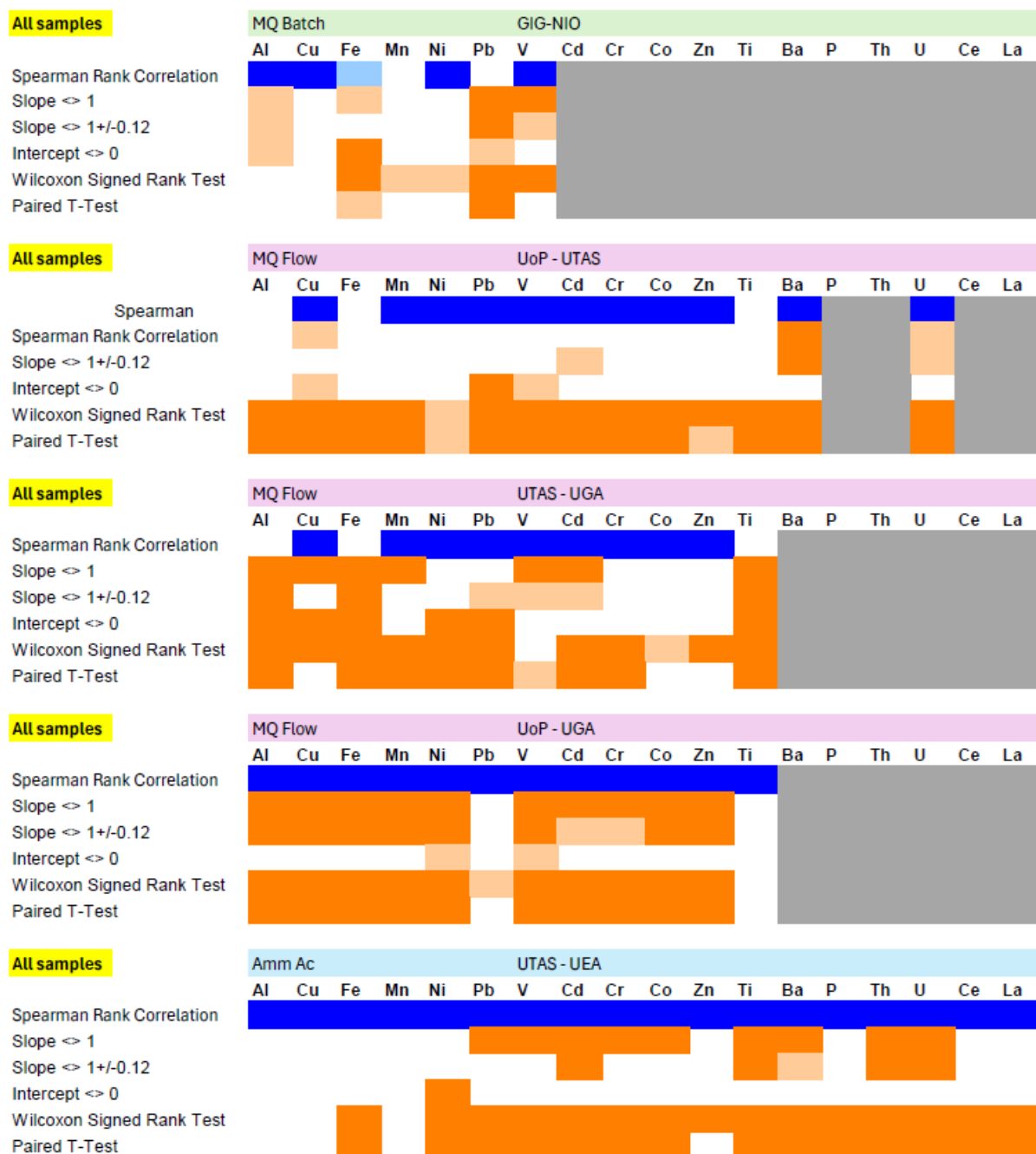
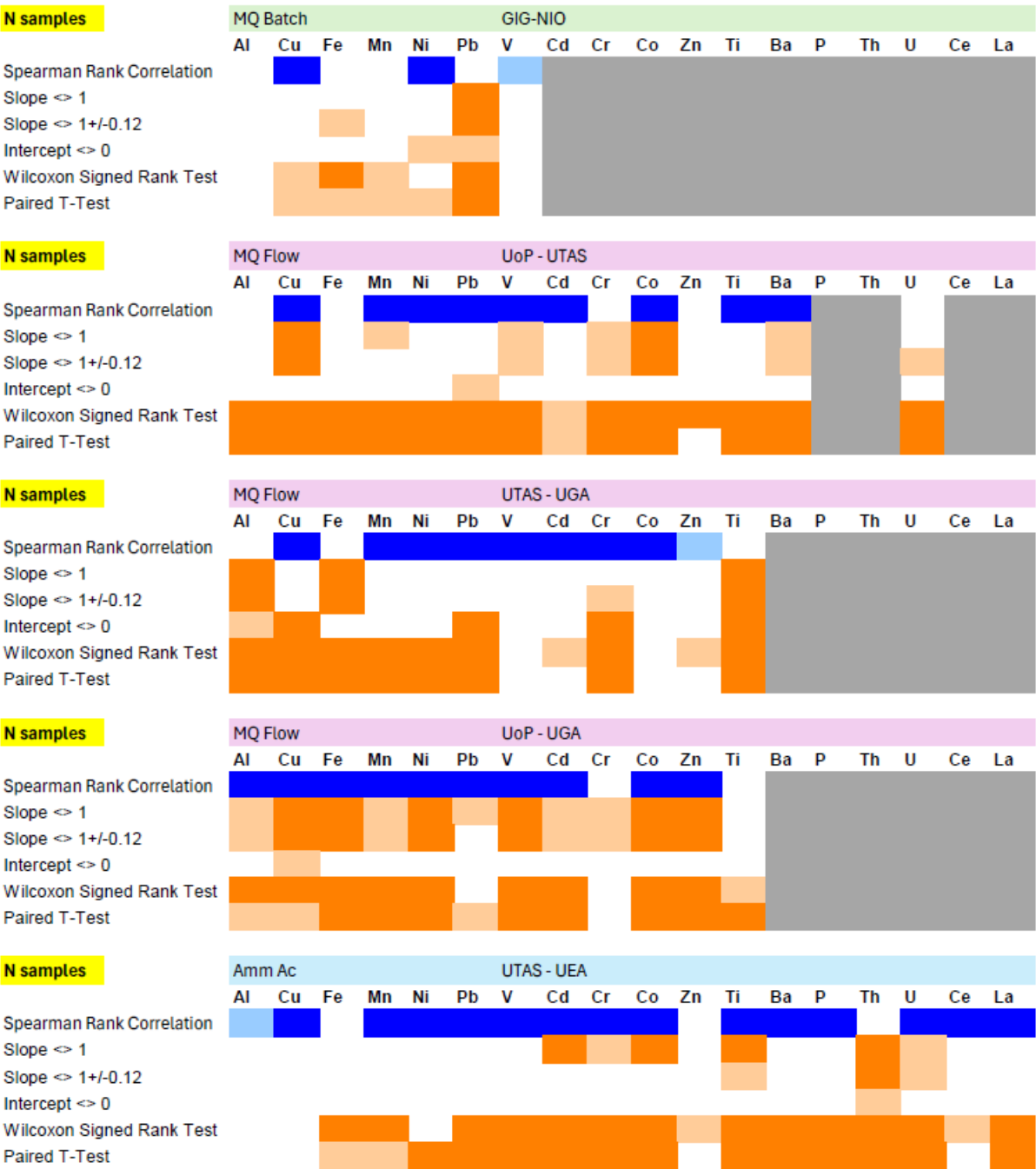


Figure S4. Summary of the statistical comparisons of the leaching methods for all of the samples (N, SW and YS) collected at Qingdao. Comparisons are only shown for similar methods: Batch UPW, Flow UPW and Ammonium Acetate. Statistical tests are described in Section 2.6.3 of the main manuscript. Significant test results are indicated by the color code (blue indicates agreement between methods, orange indicates disagreement, with lighter colors showing significance at $p < 0.05$ and darker colors $p < 0.01$). White indicates that the test result was not statistically significant. Grey indicates that element was not measured.

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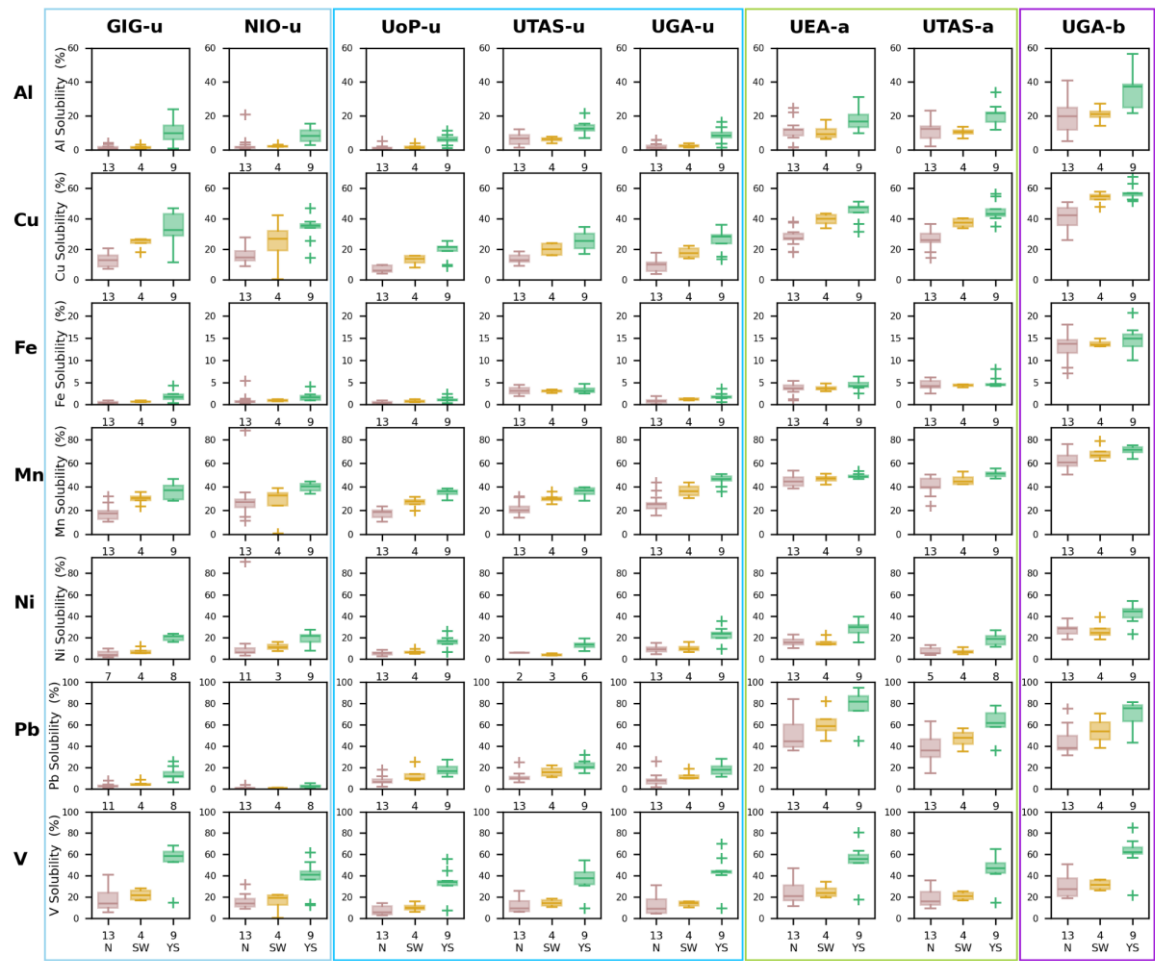


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82 **Figure S5.** Summary of the statistical comparisons of the leaching methods for the northern
83 origin (N) samples collected at Qingdao. Statistical tests and colors are as described in Figure
84 S4.



Figure S6. Summary of the statistical comparisons of the leaching methods for the marine origin (YS) samples collected at Qingdao. Statistical tests and colors are as described in Figure S4



91 **Figure S7.** Box and whisker plots of percentage solubility in N, SW and YS sample types for Al, Cu, Fe, Mn, Ni, Pb and V for all of the protocols
92 tested. Colored outlines group similar methods (as in Figure 6).

References:

- Buck, C. S., Landing, W. M., and Resing, J.: Pacific Ocean aerosols: Deposition and solubility of iron, aluminum, and other trace elements, *Marine Chemistry*, 157, 117-130, 2013.
- Buck, C. S., Landing, W. M., and Resing, J. A.: Particle size and aerosol iron solubility: A high-resolution analysis of Atlantic aerosols, *Mar. Chem.*, 120, 14-24, 2010.
- Panda, P. P., Aswini, M. A., Bhatt, P., Srimuruganandam, B., Peketi, A., and Kumar, A.: Bioactive Trace Elements' Composition and Their Fractional Solubility in Aerosols from the Arabian Sea during the Southwest Monsoon, *ACS Earth and Space Chem.*, 6, 1969-1981, 2022.
- Perron, M. M. G., Strzelec, M., Gault-Ringold, M., Proernse, B. C., Boyd, P. W., and Bowie, A. R.: Assessment of leaching protocols to determine the solubility of trace metals in aerosols, *Talanta*, 208, 120377, DOI: 120310.121016/j.talanta.122019.120377, 2020.
- Sarthou, G., Baker, A. R., Blain, S., Achterberg, E. P., Boye, M., Bowie, A. R., Croot, P., Laan, P., de Baar, H. J. W., Jickells, T. D., and Worsfold, P. J.: Atmospheric iron deposition and sea-surface dissolved iron concentrations in the eastern Atlantic Ocean, *Deep Sea Research Part I: Oceanographic Research Papers*, 50, 1339-1352, 2003.
- Zhang, H. H., Li, R., Dong, S. W., Wang, F., Zhu, Y. J., Meng, H., Huang, C. P., Ren, Y., Wang, X. F., Hu, X. D., Li, T. T., Peng, C., Zhang, G. H., Xue, L. K., Wang, X. M., and Tang, M. J.: Abundance and Fractional Solubility of Aerosol Iron During Winter at a Coastal City in Northern China: Similarities and Contrasts Between Fine and Coarse Particles, *J. Geophys. Res.-Atmos*, 127, e2021JD036070, 2022.