



1 **Aerosol trace element solubility determined using ultrapure water batch leaching: an**  
2 **intercomparison study of four different leaching protocols**

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22



23 **Abstract**

24 Solubility of aerosol trace elements, which determines their bioavailability and reactivity, is  
25 operationally defined and strongly depends on the leaching protocol used. Ultrapure water  
26 batch leaching is one of the most widely used leaching protocols, while the specific leaching  
27 protocols used in different labs can still differ in agitation methods, contact time, and filter pore  
28 size. It is yet unclear to which extent the difference in these experimental parameters would  
29 affect the aerosol trace element solubility reported. This work examined the effects of agitation  
30 methods, filter pore size and contact time on the solubility of nine aerosol trace elements, and  
31 found that the difference in agitation methods (shaking vs. sonication), filter pore size (0.22 vs.  
32 0.45  $\mu\text{m}$ ), and contact time (1 vs. 2 h) only led to small and sometimes insignificant difference  
33 in the reported solubility. We further compared aerosol trace element solubility determined  
34 using four ultrapure water leaching protocols which are adopted by four different labs and vary  
35 in agitation methods, filter pore size and/or contact time, and observed good agreement in the  
36 reported solubility. Therefore, our work suggests that although ultrapure water batch leaching  
37 protocols used by different labs vary in specific experimental parameters, the determined  
38 aerosol trace element solubility is comparable. We recommend ultrapure water batch leaching  
39 to be one of the reference leaching schemes, and emphasize that additional consensus in the  
40 community on agitation methods, contact time and filter pore size is needed to formulate a  
41 standard operating procedure for ultrapure water batch leaching.

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## 44 **1 Introduction**

45       Aerosol trace elements, originating from natural and anthropogenic sources, are of great  
46 concerns, as they significantly impact marine and terrestrial ecosystems (Boyd and Ellwood,  
47 2010; Dong et al., 2023; Mahowald et al., 2018), have adverse effects on human health  
48 (Dahmardeh Behrooz et al., 2021; Fang et al., 2017; Gao et al., 2022; Wei et al., 2019), and  
49 play important roles in atmospheric chemistry (Al-Abadleh, 2024; Alexander et al., 2009; Mao  
50 et al., 2013; Martin and Hill, 1987; Wang et al., 2021). The dissolved fraction of aerosol trace  
51 elements, instead of their total abundance, is considered to be bioavailable (Baker and Croot,  
52 2010; Ito et al., 2012; Mukhtar and Limbeck, 2013) and more chemically reactive in the  
53 atmosphere (Kebede et al., 2016; Mao et al., 2017). Dissolved trace elements are typically  
54 referred to as the fraction of elements which can pass through a filter with certain pore size  
55 (usually 0.2-0.22 or 0.45  $\mu\text{m}$ ) after aerosol particles are dissolved in certain aqueous solutions  
56 (Boyd and Ellwood, 2010; Ito and Xu, 2014; Meskhidze et al., 2016; Myriokefalitakis et al.,  
57 2018). Solubility (or fractional solubility, to be more precise), which is defined as the ratio  
58 (in %) of the dissolved element to the total element (Baker et al., 2006; Sholkovitz et al., 2012),  
59 largely determines the bioavailability and reactivity of aerosol trace elements.

60       A wide range in the solubility has been reported in the literature for a given trace element  
61 in atmospheric aerosols, and for example, the reported solubility of aerosol Fe ranges from <1%  
62 to >90% (Baker and Jickells, 2006; Sholkovitz et al., 2012). Such wide variabilities in aerosol  
63 trace element solubility, on one hand, can be caused by difference in sources and aging  
64 processes of aerosol particles examined (Ito et al., 2021; Meskhidze et al., 2019); on the other  
65 hand, they also stem from various leaching protocols which were used by different studies



66 ([Chen et al., 2006](#); [Li et al., 2023](#); [Upadhyay et al., 2011](#)).

67 Various leaching protocols have been used in previous studies to extract dissolved aerosol  
68 trace elements, as summarized in a recent paper ([Li et al., 2023](#)). In brief, available leaching  
69 protocols broadly consist of two catalogues, including flow-through leaching and batch  
70 leaching. Flow-through leaching is instantaneous and typically has a contact time (between  
71 aerosol particles and the leaching solution used) of tens of seconds, and batch leaching usually  
72 has a much longer contact time (tens of minutes or longer). Compared to flow-through leaching,  
73 batch leaching is more widely used in atmospheric research. Furthermore, for batch leaching,  
74 various leaching solutions were used in previous studies, such as ultrapure water, filtered  
75 seawater, and formate/acetate buffers. Compared to filtered seawater and formate/acetate  
76 buffers, ultrapure water is more widely used in atmospheric research due to its simplicity and  
77 reproducibility ([Li et al., 2023](#); [Meskhidze et al., 2019](#)); another important reason is that  
78 ultrapure water leaching does not introduce any other chemical species (except water) and thus  
79 can simultaneously extract water-soluble ions and organics for additional analysis.

80 Even for ultrapure water batch leaching, protocols used by different studies may still vary  
81 in agitation methods, contact time, and filter pore size; nevertheless, the effects of these factors  
82 on the reported solubility are not well understood. First, some labs use sonication to agitate the  
83 leaching solutions ([Chen et al., 2006](#); [Kumar and Sarin, 2010](#); [Liu et al., 2021](#); [Longo et al.,](#)  
84 [2016](#); [Shi et al., 2020](#)), and other labs use shaking ([Baker et al., 2003](#); [Gao et al., 2020](#); [Hsu et](#)  
85 [al., 2010](#); [Li et al., 2022](#); [Salazar et al., 2020](#)). Sonication may cause changes in chemical  
86 composition and formation of reactive oxygen species in the solution ([Juretic et al., 2015](#);  
87 [Miljevic et al., 2014](#)); however, it remains to be examined whether sonication will change the



88 solubility of aerosol trace elements. Second, filters with different pore sizes, including 0.2-0.22  
89 and 0.45  $\mu\text{m}$  (and 0.02  $\mu\text{m}$  to a less extent), are employed to filter the leaching solutions,  
90 contributing to the uncertainties in the reported solubility; however, the effects of filter pore  
91 size have seldom been experimentally examined. Third, some studies (Li et al., 2023; Mackey  
92 et al., 2015) suggested that contact time (2-8 h) could also influence the reported solubility.

93 In the present work, using aerosol particles collected at a suburban site close to the  
94 coastline of the Northwest Pacific, we investigated to which extent different ultrapure water  
95 batch leaching protocols would affect reported aerosol trace element solubility. In the first part  
96 of this work, we examined the effects of agitation (shaking vs. sonication), filter pore size (0.22  
97 vs. 0.45  $\mu\text{m}$ ) and contact time (1 vs. 2 h) on the reported solubility of nine aerosol trace elements.  
98 In the second part, we compared solubility determined using protocols commonly adopted by  
99 four labs. The four labs all use ultrapure water batch leaching, but the leaching protocols they  
100 use differ in agitation method, contact time, and/or filter pore size.

## 101 **2 Experimental section**

### 102 **2.1 Sample collection and distribution**

103 We collected aerosol samples between 18 March and 22 April 2023 in Qingdao, a coastal  
104 city in northern China, typically impacted by desert dust and anthropogenic aerosols in spring.  
105 As described elsewhere (Zhang et al., 2022), aerosol sampling took place at a suburban site  
106 which was about 1.3 km from the coast. A custom-made high-volume aerosol sampler (ASM-  
107 1; flow rate: 1  $\text{m}^3/\text{min}$ ) was deployed on a building roof (about 20 m above the ground) to  
108 collect  $\text{PM}_{10}$  samples. Aerosol sampling started at 08:00 am each day and stopped at 07:30 am  
109 on the next day, resulting in a sampling volume of 1410  $\text{m}^3$ .  $\text{PM}_{10}$  samples were collected onto



110 pre-cleaned Whatman 41 cellulose fiber filters (25 cm × 20 cm) which had very low  
111 backgrounds for trace elements (Morton et al., 2013; Zhang et al., 2022). In total we collected  
112 26 filter samples, 4 sampling blanks, and 3 lab blanks: lab blanks were defined as pre-cleaned  
113 filters, and sampling blanks were defined as pre-cleaned filters which were placed in the aerosol  
114 sampler for 2 h when the sampling flow was off.

115 After aerosol collection, each filter was folded inward and placed into a clean  
116 polyethylene bag (12 inch × 9 inch, supplied by Sigma-Aldrich) which was used due to its low  
117 background (Morton et al., 2013), and then stored at -20 °C. A titanium punch was used to  
118 obtain 10 subsamples (47 mm in diameter) from each filter sample, and these subsamples were  
119 stored at -20 °C.

## 120 2.2 Measurement of total and dissolved trace elements

### 121 2.2.1 Total elements

122 As shown in Table 1 and described below, for the 10 subsamples obtained from each  
123 original filter sample, the first subsample was digested to determine total elements, another  
124 eight subsamples were leached using different protocols to determine dissolved elements, and  
125 the last subsample was reserved for any unforeseen purpose (but was not used at the end).

126 Subsample 1 was digested in a Teflon jar which contained a mixture of HNO<sub>3</sub>-HF-H<sub>2</sub>O<sub>2</sub>,  
127 using a microwave digestion system (Zhang et al., 2022). After digestion, we evaporated  
128 residual acids in the Teflon jar, and filled it with 20 mL HNO<sub>3</sub> (1%). Subsequently, we filtered  
129 the solution through a polyethersulfone membrane syringe filter (with a pore size of 0.22 μm),  
130 and then used ICP-MS (inductively coupled plasma mass spectrometry, iCAP Q, Thermo  
131 Fisher) to measure nine trace elements, including Fe, Al, As, Cr, Cu, Mn, Pb, V and Zn.



132

133 **Table 1.** Overview of protocols used to digest and leach subsamples examined in this work.

subsample	agitation	contact time (h)	filter pore size ( $\mu\text{m}$ )	Lab	References
1	digestion			GIG	
2a	shaking	2	0.22	GIG	<a href="#">Zhang et al. (2022)</a>
2b	shaking	2	0.22	GIG	
2c	shaking	2	<b>0.45</b>		
2d	<b>sonication</b>	2	0.22		
2e	shaking	<b>1</b>	0.22		
3a	sonication	1	0.22	ZJU	<a href="#">Liu et al. (2021)</a>
3b	sonication	1	0.45	OUC	<a href="#">Shi et al. (2020)</a>
3c	sonication	0.5	0.20	NIO	<a href="#">Panda et al. (2022)</a>

134

### 135 2.2.2 Dissolved elements

136 Subsample 2a was leached using the protocol adopted by the lab at Guangzhou Institute  
137 of Geochemistry (GIG) ([Li et al., 2023](#); [Zhang et al., 2022](#); [Zhang et al., 2023](#)). In brief, the  
138 subsample was shredded and then immersed in 20 mL ultrapure water for 2 h, stirred using an  
139 orbital shaker; subsequently, the solution was filtered through a polyethersulfone membrane  
140 syringe filter (with a pore size of 0.22  $\mu\text{m}$ ). After that, the solution was immediately acidified  
141 with a small volume of high-purity  $\text{HNO}_3$  to contain 1%  $\text{HNO}_3$ , and then analyzed using ICP-  
142 MS to determine dissolved trace elements. Subsample 2b was leached using the same protocol  
143 as subsample 2a, and the purpose was to examine whether aerosol particles were  
144 homogeneously distributed on different subsamples, and to assess the repeatability of the GIG  
145 leaching protocol.



146           Subsamples 2c-2e were leached using protocols similar to that used to leach subsample  
147 2a. As summarized in Table 1, the only difference to the protocol used to leach subsample 2a  
148 was the filter pore for 2c (0.45  $\mu\text{m}$ , vs. 0.22  $\mu\text{m}$  for 2a), agitation method for 2d (sonication, vs.  
149 shaking for 2a), and contact time for 2e (1 h, vs. 2 h for 2a). The purpose of using subsamples  
150 2c-2e is to examine the effects of filter pore size (0.22 vs. 0.45  $\mu\text{m}$ ), agitation method (shaking  
151 vs. agitation), and contact time (1 vs. 2 h) on the reported solubility.

152           Subsamples 3a, 3b and 3c were leached using the protocols typically used by ZJU  
153 (Zhejiang University, China), OUC (Ocean University of China, China) and NIO (National  
154 Institute of Oceanography, India), respectively, in order to compare solubility determined by  
155 the GIG lab with those reported by the other three labs. Please note that subsamples 3c were  
156 leached and analyzed by NIO, while subsamples 3b and 3c were leached and analyzed at GIG  
157 (using the ZJU and OUC protocols, respectively).

158           Subsample 3a was leached at GIG using the ZJU protocol (Liu et al., 2021; Zhu et al.,  
159 2020). In brief, each subsample was shredded and immersed in 20 mL ultrapure water, and the  
160 aqueous mixture was sonicated for 1 h during which the water bath temperature was kept below  
161 30 °C; after that, the aqueous mixture was filtered using a polyethersulfone membrane syringe  
162 filter (pore size: 0.22  $\mu\text{m}$ ) and acidified for later ICP-MS analysis. Subsample 3b was leached  
163 at GIG using the OUC protocol (Shi et al., 2020), which is very similar to the ZJU method: the  
164 only difference is that the filter pore size was 0.45  $\mu\text{m}$  for the OUC protocol and 0.22  $\mu\text{m}$  for  
165 the ZJU protocol.

166           Subsample 3c was leached and analyzed at NIO using the NIO protocol (Panda et al.,  
167 2022). In brief, each subsample was shredded and placed into a pre-cleaned Savillex vial (50





168 mL); after that, the vial was filled with 20 mL ultrapure water, capped, and then sonicated for  
169 30 minutes to agitate the aqueous mixture (but in 2 cycles with 15 min for each cycle, in order  
170 to maintain the water bath at room temperature). The aqueous mixture was then filtered through  
171 a Whatman PVDF syringe filter (pore size: 0.2  $\mu\text{m}$ ), and then acidified with  $\text{HNO}_3$  (2% v/v)  
172 for later high-resolution ICP-MS analysis (Nu Instruments, Attom ES).

### 173 **3 Results and discussion**

174 Subsamples 2a and 2b were identically leached using the protocol GIG normally uses, and  
175 the paired  $t$ -test ( $\alpha = 0.05$ ) was employed to examine whether the difference in obtained  
176 solubility was significant. As summarized in Table 2, the difference in obtained solubility was  
177 not statistically significant between 2a and 2b for Fe, Al, As, Mn, Pb, and V; furthermore,  
178 Figure S1 suggests good linear correlations in solubility between 2a and 2b for the six elements  
179 ( $R > 0.99$ ), and the corresponding slopes (0.98 to 1.02) were very close to 1. For the other three  
180 elements (Cr, Cu and Zn), although the difference in solubility was found to be statistically  
181 significant between 2a and 2b (Table 1), good linear correlations between the solubility were  
182 found ( $R > 0.97$ ) and the slopes (1.00-1.06) were close to 1; therefore, the difference in  
183 solubility between 2a and 2b, if it existed, was small for Cr, Cu and Zn.

184 In summary, we conclude that the distribution of aerosol particles on a given original filter  
185 was homogeneous and that the protocol GIG normally uses had very good repeatability.

186

187 **Table 2.** Summary of statistical analysis (paired- $t$ -test,  $\alpha = 0.05$ ) which examined whether the  
188 difference in solubility obtained for different groups of subsamples is statistically significant.  
189 Solubility obtained for subsamples 2a is compared with those obtained for subsamples 2b, 2c,



190 2d and 2e, respectively. Y: the difference is statistically different; N: the difference is not  
191 statistically different.

element	2a vs. 2b	2a vs. 2c	2a vs. 2d	2a vs. 2e
Fe	N	<u>Y</u>	<u>Y</u>	<u>Y</u>
Al	N	N	N	<u>Y</u>
As	N	N	<u>Y</u>	<u>Y</u>
Cr	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
Cu	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>
Mn	N	N	<u>Y</u>	<u>Y</u>
Pb	N	<u>Y</u>	<u>Y</u>	N
V	N	N	N	N
Zn	<u>Y</u>	<u>Y</u>	<u>Y</u>	<u>Y</u>

192

### 193 3.1 The effects of filter pore size

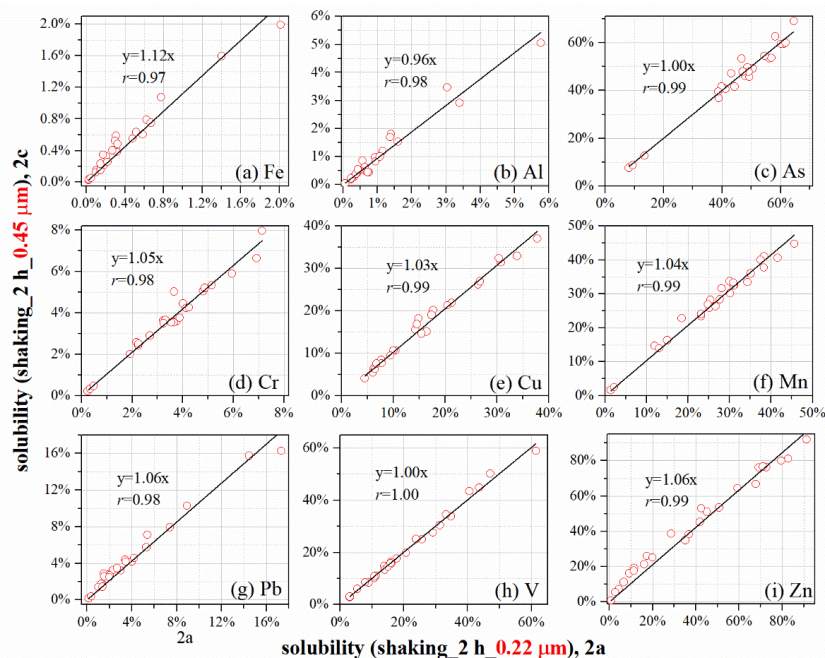
194 To examine the effects of filter pore size on the reported solubility, subsamples 2a and 2c  
195 were leached using very similar protocols, and the only difference is the pore size (2a: 0.22  $\mu\text{m}$ ;  
196 2c: 0.45  $\mu\text{m}$ ) of filters used (Table 1).

197 The difference in obtained solubility was not statistically significant between 2a and 2c  
198 for Al, As, Mn and V (Table 2); moreover, good linear correlations between 2a and 2c were  
199 found for the four elements (Figure 1), with slopes (0.96-1.04) very close to 1. For the other  
200 five elements (Fe, Cr, Cu Pb, and Zn), the difference in solubility between 2a and 2c was found  
201 to be statistically significant; however, solubility between 2a and 2c was very well linearly  
202 correlated (Figure 1), with slopes (1.03-1.12) close to or slightly larger than 1.

203 To conclude, among the nine elements we examined, the effects of filter pore size (0.22  
204 vs. 0.45  $\mu\text{m}$ ) on reported solubility were found to be insignificant for four elements (Al, As,



205 Mn and V) and very smaller for the other five elements (Fe, Cr, Cu, Pb and Zn).



206

207 **Figure 1.** The effects of filter pore size (2a: 0.22  $\mu\text{m}$ ; 2c: 0.45  $\mu\text{m}$ ) on measured element  
208 solubility. The only difference in protocols used to leach subsamples 2a and 2c is the filter pore  
209 size (0.22 versus 0.45  $\mu\text{m}$ ).

210

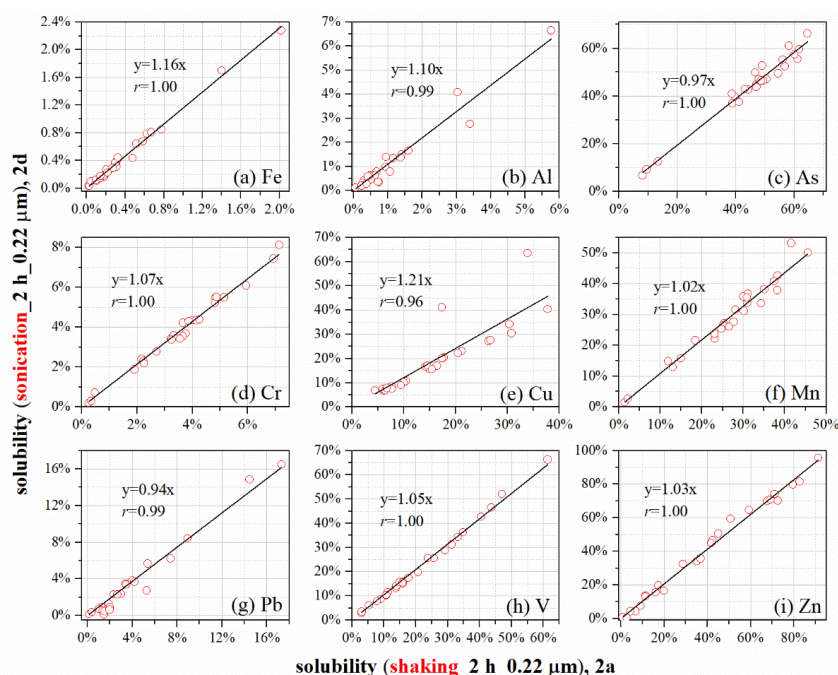
### 211 3.2 The effects of agitation

212 As shown in Table 1, the only difference between the protocol used to leach subsamples  
213 2a and that used to leach subsamples 2d is the agitation method used (2a: shaking; 2d:  
214 sonication), and solubility obtained for subsamples 2a and 2d was compared to assess the  
215 effects of agitation methods on reported solubility.

216 Table 2 shows that the reported solubility between 2a and 2d was not statistically different  
217 for two elements (Al and V); in addition, good linear correlations between 2a and 2d were



218 found for the two elements (Figure 2), and these slopes (1.10 for Al and 1.05 for V) were quite  
219 close to 1. With respect to the other seven elements (Fe, As, Cr, Cu, Mn, Pb and Zn), on one  
220 hand, the difference in solubility between 2a and 2d was found to be statistically significant;  
221 on the other hand, good linear correlations in solubility existed between 2a and 2d (Figure 2),  
222 and these slopes were in the range of 0.94-1.21.



223  
224 **Figure 2.** The effects of agitation (2a: shaking; 2d: sonication) on measured element solubility.  
225 The only difference in protocols used to leach subsamples 2a and 2d is the agitation method  
226 (shaking vs. sonication).

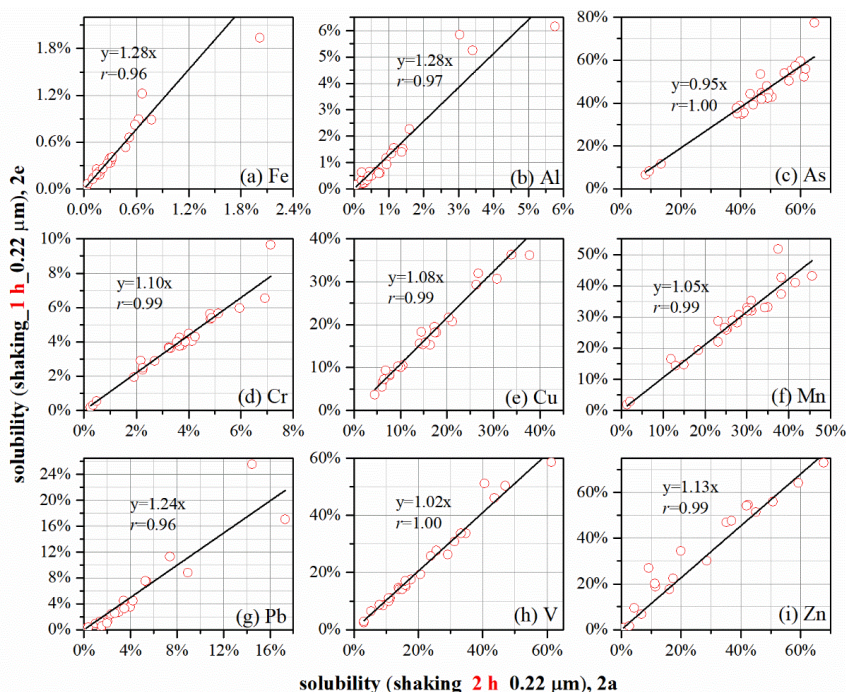
227  
228 In summary, we found that the choice of agitation methods (shaking vs. sonication) had  
229 no measurable (for Al and V) or small effects (for Fe, As, Cr, Cu, Mn, Pb and Zn) on the  
230 reported solubility.



### 231 3.3 The effects of contact time

232 To assess the impacts of contact time on reported solubility, subsamples 2a and 2e were  
233 leached using very similar protocols, and the only difference was contact time (2a: 2 h; 2e: 1 h).

234 As shown in Table 2, the reported solubility were not statistically different between 2a  
235 and 2e for Pb and V; moreover, good linear relationships between 2a and 2e were found for the  
236 two elements (Figure 3), with slopes close to 1 (1.24 for Pb and 1.02 for V). For the other seven  
237 elements, their solubility was found to be statistically significant between 2a and 2e (Table 2);  
238 nevertheless, for each of the seven elements, the solubility reported for 2a was very well  
239 linearly correlated with that reported for 2e (Figure 3), and the slopes were close to 1 (in the  
240 range of 0.95-1.28).



241



242 **Figure 3.** The effects of contact time (2a: 1 h; 2e: 2 h) on measured element solubility. The  
243 only difference in protocols used to leach subsamples 2a and 2e is the contact time (1 h versus  
244 2 h).

245

246 To summarize, our present work suggested that the increase in contact time from 1 h to 2  
247 h would cause insignificant or small effects on reported solubility. Using a different set of  
248 aerosol samples, our previous work (Li et al., 2023) compared the measured solubility obtained  
249 with longer contact time (4 and 8 h) to that obtained with a contact time of 2 h. As shown in  
250 Table S1, increase in contact time from 2 to 4 h would cause significant increase in solubility,  
251 on average by a factor of ~1.3 for Zn to ~3.1 for As (Li et al., 2023). It is still not clear why the  
252 increase in contact time from 1 to 2 h would not cause significant change in aerosol trace  
253 element solubility while the increase in contact time from 2 to 4 h would.

#### 254 **3.4 Comparison of solubility obtained using protocols commonly used by four labs**

255 We further compared solubility determined using the GIG protocol with those determined  
256 using ZJU, OUC and NIO protocols, respectively. Table 3 summarizes the slopes obtained from  
257 correlation analysis (Figures 4 and S2-S8). The NIO lab measured eleven elements, among  
258 which five elements (Fe, Al, Cu, Mn, and V) were measured using the other three protocols; as  
259 a result, the solubility of these five elements determined using the NIO protocol was compared  
260 with those determined using the GIG protocol.

261

262 **Table 3.** Correlations between solubility determined using the GIG protocol and that  
263 determined using ZJU, OUC and NIO protocols. Here only the slopes ( $k$ ) are provided.



	ZJU	OUC	NIO
	<i>k</i>	<i>k</i>	<i>k</i>
Fe	1.03	1.39	1.82
Al	1.09	1.19	1.80
As	0.96	0.87	--
Cr	0.96	0.97	--
Cu	1.06	1.04	0.99
Mn	0.99	0.98	1.09
Pb	0.97	1.01	--
V	1.06	0.99	1.05
Zn	0.97	0.94	--

264

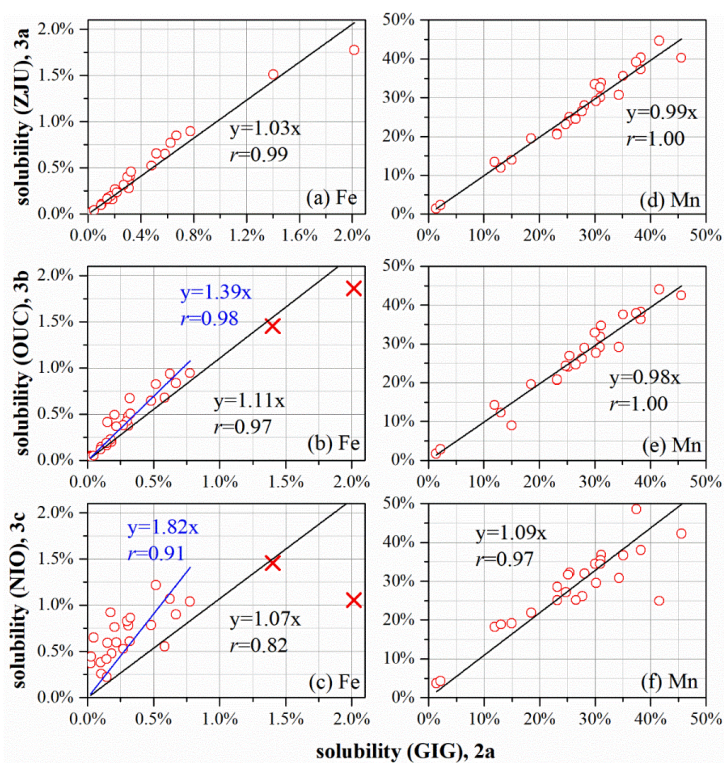
265 With respect to Fe solubility, GIG results were very well correlated with ZJU results ( $r =$   
266 0.99, Figure 4a) and the slope was found to be 1.03, suggesting good agreement between GIG  
267 and ZJU; GIG results were also well correlated with while overall larger than OUC results ( $r$   
268 = 0.98, Figure 4b), and the slope was determined to be 1.39; good correlation was also found  
269 between GIG and NIO results ( $r = 0.91$ , Figure 4c), and the slope was determined to be 1.82,  
270 indicating that Fe solubility determined using the NIO protocol was larger than that determined  
271 using the GIG protocol. Similarly, with respect to Al solubility (Figure S2 and Table 3), the  
272 GIG results were well correlated with ZJU, OUC and NIO results, and correlations were best  
273 for ZJU ( $r = 0.99$ ) and moderate for NIO ( $r = 0.93$ ); in addition, the slopes were determined to  
274 be 1.09, 1.19 and 1.80 for ZJU, OUC and NIO results, respectively.

275 With respect to Cu (Figure S5), Mn (Figures 4d-4f) and V (Figure S7), their solubility  
276 determined using the ZJU, OUC and NIO protocols was well correlated with that determined  
277 using the GIG protocol, and the slopes obtained from correlation analysis, which ranged from  
278 0.98 to 1.09 (Table 3), were all close to 1.

279 Since As, Cr, Pb and Zn were not measured using the NIO protocol, we only compared  
280 GIG results with ZJU and OUC results for these four elements. As shown in Figures S3, S4,



281 S6 and S8, the solubility of As, Cr, Pb and Zn determined using ZJU and OUC protocols was  
282 well correlated with that determined using the GIG protocol, and the slopes (0.87-1.01, as  
283 summarized in Table 3) were close to 1.



284  
285 **Figure 4.** Solubility of Fe and Mn determined using the GIG protocol vs. those determined  
286 using ZJU, OUC and NIO protocols: (a) Fe, GIG vs. ZJU; (b) Fe, GIG vs. OUC; (c) Fe, GIG  
287 vs. NIO; (d) Mn, GIG vs. ZJU; (e) Mn, GIG vs. OUC; (f) Mn, GIG vs. NIO.

288  
289 To summarize, although the four ultrapure water batch leaching protocols differ in  
290 agitation method, contact time and/or filter pore size (GIG: shaking, 2 h contact time, 0.22  $\mu\text{m}$   
291 filter pore size; ZJU: sonication, 1 h contact time, 0.22  $\mu\text{m}$  filter pore size; OUC: sonication, 1  
292 h contact time, 0.45  $\mu\text{m}$  filter pore size; NIO: sonication, 1 h contact time, 0.22  $\mu\text{m}$  filter pore





293 size), for the nine elements examined in this intercomparison study, their solubility determined  
294 using the four protocols in general showed good agreement. This is consistent with the results  
295 presented in Sections 3.1-3.3, where we found that the effects of agitation method (shaking vs.  
296 sonication), contact time (1 vs. 2 h) and filter pore size (0.22 vs. 0.45  $\mu\text{m}$ ) were rather limited.  
297 The solubility of Fe and Al determined using the NIO protocol deviated considerably from  
298 those determined using the GIG protocol, probably because Fe and Al solubility was very low  
299 (mostly <2%) and small change in leaching protocol may cause significant change in the  
300 amounts of Fe and Al dissolved.

#### 301 **4 Conclusion**

302       Ultrapure water batch leaching is widely used in atmospheric research to determine  
303 aerosol trace element solubility, and the specific leaching protocols used in different labs can  
304 still vary in agitation methods, contact time, and filter pore size. It is yet unclear to which extent  
305 the difference in these experimental parameters would affect the reported aerosol trace element  
306 solubility; in other words, it remains to be examined whether solubility reported by previous  
307 studies which used different ultrapure water batch leaching protocols is comparable.

308       We examined the effects of agitation methods, filter pore size and contact time on the  
309 reported solubility of nine aerosol trace elements, including Fe, Al, As, Cr, Cu, Mn, Pb, V and  
310 Zn. It was found that the difference in agitation methods (shaking vs. sonication), filter pore  
311 size (0.22 vs. 0.45  $\mu\text{m}$ ), and contact time (1 vs. 2 h) only led to small and sometimes  
312 insignificant difference in the reported solubility. We further compared aerosol trace element  
313 solubility determined using four widely used ultrapure water leaching protocols which differ  
314 in agitation methods, filter pore size and/or contact time, and in general the solubility



315 determined using the four protocols was found to be in good agreement. Therefore, aerosol  
316 trace element solubility determined in previous studies using ultrapure water batch leaching  
317 may be comparable.

318 Aerosol trace element solubility is an operationally defined term (Baker and Croot, 2010;  
319 Meskhidze et al., 2019), and strongly depends on the leaching protocol employed. A number  
320 of leaching protocols have been used in previous studies to extract dissolved trace elements,  
321 making it very challenging to compare solubility reported in different studies (Perron et al.,  
322 2024). In order to reduce uncertainties in aerosol trace element solubility, it is necessary to  
323 formulate standard operating procedures for frequently-used aerosol leaching protocols. Our  
324 current work suggests that although ultrapure water batch leaching protocols used by different  
325 labs vary in specific experimental parameters, the determined aerosol trace element solubility  
326 showed good agreement; furthermore, ultrapure water batch leaching is operationally simple  
327 and does not introduce any other chemical species which may interfere analysis of water-soluble  
328 inorganic ions and organics. Therefore, we recommend ultrapure water batch leaching to be  
329 one of the reference leaching schemes. Before a standard operating procedure can be  
330 formulated for ultrapure water batch leaching, the community will need to reach consensus on  
331 agitation methods, contact time and filter pore size, and further intercomparison studies,  
332 preferentially with more labs involved, will be very helpful.

333

334 **Data availability.**

335 Data are available upon request (Mingjin Tang: mingjintang@gig.ac.cn).

336 **Author contributions.**



337 [Rui Li](#): methodology, formal analysis, investigation, writing - original draft, writing - review  
338 & editing; [Prema Piyusha Panda](#): formal analysis, investigation; [Yizhu Chen](#): investigation;  
339 [Zhenming Zhu](#): investigation; [Fu Wang](#): investigation, supervision; [Yujiao Zhu](#): resources; [He](#)  
340 [Meng](#): resources; [Yan Ren](#): resources, supervision; [Ashiwini Kumar](#): resources, writing -  
341 review & editing, supervision; [Mingjin Tang](#): conceptualization, methodology, resources,  
342 writing - original draft, writing - review & editing, supervision.

343 **Competing interests.**

344 Mingjin Tang is a member of the editorial board of Atmospheric Measurement Techniques.

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