

1 **Evaluation of airborne particulate matter and metals data in personal, indoor and outdoor**
2 **environments using ED-XRF and ICP-MS and co-located duplicate samples**

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9 **Abstract**

10 Factors and sources affecting measurement uncertainty associated with monitoring metals in
11 airborne particulate matter (PM) were investigated as part of the Windsor, Ontario Exposure
12 Assessment Study (WOEAS). The assessment was made using co-located duplicate samples and
13 a comparison of two analytical approaches: ED-XRF and ICP-MS. Sampling variability was
14 estimated using relative percent difference (RPD) of co-located duplicate samples. The
15 comparison of ICP-MS and ED-XRF results yields very good correlations ($R^2 \geq 0.7$) for elements
16 present at concentrations that pass both ICP-MS and ED-XRF detection limits (e.g. Fe, Mn, Zn,
17 Pb and Cu). PM concentration ranges (median, sample number) of 24-hr indoor PM₁₀ and
18 personal PM₁₀ filters, and outdoor PM_{2.5} filters were determined to be 2.2 –40.7 (11.0, n= 48) μg
19 m^{-3} , 8.0 - 48.3 (11.9, n= 48) $\mu\text{g m}^{-3}$, and 17.1 – 42.3 (21.6, n=18)) $\mu\text{g m}^{-3}$, respectively. The
20 gravimetric analytical results reveal that the variations in PM mass measurements for same-day
21 sampling are insignificant compared to temporal or spatial variations: 92%, 100% and 96% of
22 indoor, outdoor and personal duplicate samples, respectively, pass the quality criteria (RPD \leq
23 20%). Uncertainties associated with ED-XRF elemental measurements of S, Ca, Mn, Fe and Zn
24 for 24-hr filter samples are low: 78% to 100% of the duplicate samples pass the quality criteria. In

25 the case of 24-hr filter samples using ICP-MS, more elements passed the quality criteria due to the
26 lower detection limits. These were: Li, Na, K, Ca, Si, Al, V, Fe, Mn, Co, Cu, Mo, Ag, Zn, Pb, As,
27 Mg, Sb, Sn, Sr, Th, Ti, Tl, and U. Low air concentrations of metals (near or below instrumental
28 detection limits) and/or inadvertent introduction of metal contamination are the main causes for
29 excluding elements based on the pass/fail criteria. Uncertainty associated with elemental
30 measurements must be assessed on an element-by-element basis.

31 *Keywords:* Particulate matter; Uncertainty; Metals; Exposure Assessment; Air pollution; ICP-MS;
32 ED-XRF

33 **1. Introduction**

34 Air pollutants, especially airborne particulate matter (PM) and metals in PM, have been associated
35 with both short-term and long-term adverse health effects including chronic respiratory disease,
36 heart disease, lung cancer, and damage to other organs (Costa et al., 1997; Ghio et al., 1999; Allen
37 et al., 2001; Vincent et al., 2001; Frieditis et al., 2002; Osonio-Vargas et al., 2003; Rasmussen,
38 2004; Lingard et al., 2005; Williams et al., 2007; Niu et al., 2008). Characterization of PM
39 components, including inorganic elements, is of central importance in proposing mechanisms for
40 health effects and in source apportionment studies (Butler et al., 2008, 2009). One of the most
41 effective strategies to address the increasing public concern from criteria air pollutants and their
42 impact on human health is through undertaking personal exposure monitoring. The Windsor,
43 Ontario Exposure Assessment Study (WOEAS; Williams et al., 2007), launched in 2005, aims to
44 provide accurate and representative human exposure data collected across the city for indoor and
45 outdoor residential locations, and personal environments. To meet the study goals of WOEAS,
46 development of accurate and reliable sampling approaches is a critical focus, since sampling
47 variability is one of the most important contributors to the overall uncertainty of exposure

48 measurements of PM and PM-bound transition metals. Efforts in this area are essential to obtain
49 accurate and representative information on daily exposures of urban populations to air pollution.

50 At the outset of the Windsor sampling program, a pilot study of 24-hr personal, indoor and
51 outdoor levels of PM_{2.5} and associated metals was conducted to develop standard operating
52 procedures for field sampling and laboratory analysis (Rasmussen et al., 2007a). The present
53 study is a continuation of this effort to improve monitoring quality, by using co-located duplicate
54 samples to identify uncertainties associated with monitoring PM-bound metals. Recently
55 Lippmann (2009) identified the need for such information, pointing out that problems in
56 interpretation may arise from readings of elements in airborne PM which are near or below the
57 lower detection limits. The aim of using co-located duplicate PM samples is to unravel all the
58 sources of uncertainty in the multi-element data and to provide a framework for assessing such
59 uncertainties as part of the larger monitoring study in Windsor Ontario. Effective quality control
60 criteria were developed to assess data derived from integrated 24-hr personal and indoor PM₁₀
61 samples, and 2-week outdoor PM_{2.5} samples.

62 There are many challenges in the WOEAS approach. One is the small particle mass collected on
63 the filter samples due to the short sampling time (24 hours) and the low flow rates (4 LPM) (Niu
64 et al., 2007a; Rasmussen et al., 2007b). A 24-hr sampling time was employed in the present study
65 as 24-hr measurements are the standard in the majority of air pollution guidelines (US EPA, 2006;
66 CESI, 2008). Light-weight battery-operated low-flow samplers are required for personal
67 monitoring, and to minimize noise and disruption during indoor monitoring, while the participants
68 are carrying out their normal daily routines (Rasmussen et al, 2006a; 2007a). Although there are
69 many advantages to recently developed real-time PM monitoring techniques (Butterfield and
70 Quincey, 2007), gravimetric analysis techniques remain important for studies involving
71 characterization of PM-bound metals. In addition, there is a continued requirement for accurate

72 and reliable 24-hr PM sampling as a comparison method to calibrate continuous monitoring
73 techniques (Lanki et al., 2002; Lippmann, 2009).

74 The low sample mass pose a major obstacle in obtaining reliable elemental data, as many metals
75 (particularly those present in trace concentrations in the airborne particles) are below the detection
76 limits of the Energy Dispersive X-ray Fluorescence (ED-XRF) spectrometer, as observed in a
77 preliminary residential air study in Ottawa (Rasmussen et al., 2006a). Problems associated with
78 using the more sensitive and increasingly popular Inductively Coupled Plasma Mass Spectroscopy
79 (ICP-MS) approach arise not from the instrumental detection limits but from issues related to
80 sampling and analysis: sample contamination during collection, processing, transporting,
81 weighing, extraction/digestion, and analysing procedures.

82 Challenges also arise from data correlation and equivalence (Butterfield and Quincey, 2007)
83 between different science-based techniques which sometimes show bias or even unrelated results
84 for PM monitoring (Lanki et al., 2002; Braniš and Hovorka, 2005). Both ED-XRF and ICP-MS
85 are commonly employed but fundamentally different techniques for analysing PM-bound
86 elements. Thus, data comparability between these methods is an important issue. There is very
87 limited work on comparisons of ED-XRF and ICP-MS (Herner et al., 2006). A direct and detailed
88 data correlation study to determine the degree to which the air quality data obtained using ICP-
89 MS can be compared with ED-XRF in the present study will be helpful to address the information
90 gap in this field.

91 The present study establishes the relative advantages and limitations of each instrumental
92 approach, but goes further to demonstrate that the capacity of the field and lab personnel to collect
93 and maintain uncontaminated samples during the whole measurement process (from sampling to
94 analysis) is critical. Most epidemiological studies investigating health effects of airborne metals

95 rely on occupational data (e.g. Wild et al. 2009), due to the current lack of reliable population-
96 based airborne metals data. The few epidemiological studies of metals in urban air which have
97 been published (e.g. Hibbs, 2002) would be more likely to be incorporated into risk assessments if
98 the analytical and sampling uncertainties were better quantified and constrained. As future urban
99 air studies are undertaken to address the airborne metals data gap, researchers will be increasingly
100 obligated to monitor and report quality assurance data if the results are to be accepted as valid by
101 regulators and risk managers. Uncertainty arising from sampling variability, the first stage of a
102 measurement (Ramsey et al., 1997), is an issue of great concern due to its major contribution to
103 the overall measurement uncertainty (Ramsey et al., 1995, 1997; Horowitz et al., 1997; Jorhem et
104 al., 2006; Rasmussen et al., 2006a; Niu et al., 2007a). There is very scarce information for
105 identification of metal contamination and related sources. The present study focuses on this field
106 to provide helpful information for evaluating data reliability to obtain accurate and reliable results
107 for PM-bound elements analysis.

108 **2. Experimental**

109 *2.1. Field Sampling*

110 Regular and duplicate samples for 24-hr or two-week periods were collected (Table 1). The
111 integrated non-duplicate 24-hr personal and indoor samples of PM_{2.5} and PM₁₀ were collected
112 using the R & P ChemPassTM multi-pollutant sampler and BGI 400 Personal Sampling Pumps at a
113 flow rate of 4 L min⁻¹. Three adult participants wore Personal Environmental Monitors (PEMs)
114 (Demokritou et al., 2001) for 4 consecutive days. Each backpack contained two PEMs with one
115 pump for each of them and each pump was configured with two PM₁₀ samplers. Duplicate
116 stationary monitors were placed inside three Windsor homes for the same 4-day period with the
117 same double PM₁₀ sampler configuration.

118 Samples of PM_{2.5} were also collected simultaneously over a two-week period (Aug. 3-17, 2005)
119 using PEMs at low flow rates (1.8 L min⁻¹) from the backyards of Windsor residences. A total of
120 42 two-week individual samples (including 3 field blanks) and 9 two-week duplicate PM_{2.5}
121 samples were collected.

122 To assess uncertainties of both gravimetric and elemental measurements associated with the field
123 monitoring, a duplicate study was conducted using 24-hr duplicate samples (48 indoor, 18
124 outdoor, and 48 personal (Table 1)) which were collected by setting up monitors at 4 L min⁻¹.

125 Teflon filters (37-mm with PTFE ring support) were used for all sampling campaigns. The PEM
126 filter assemblies were prepared and dismantled at the University of Windsor using nitrile gloves
127 and PTFE coated forceps. The Teflon filters were changed and shipped to Health Canada after
128 sampling for gravimetric analysis. The impactors were cleaned and impaction plates were
129 recoated after every sample, and a drain disk was placed on top of the stainless-steel screen to
130 minimize contact between the filter and the aluminum filter holder.

131 2.2. *Quality assurance*

132 Extreme precautions were taken to avoid any inadvertent contamination of filter samples during
133 all steps of handling and processing. Field blanks, laboratory filter blanks, gravimetric analysis
134 blanks, reagent blanks and NIST certified reference materials (Table 1) were used to monitor
135 potential sources of contamination, instrument performance, analytical accuracy and precision.

136 A wide range of NIST certified reference materials, including Urban Particulate Matter (NIST
137 1648), Indoor Dust (NIST 2583 and NIST 2584), Coal Fly Ash (NIST 1633b), Urban Soil (NIST
138 2586), Suburban Soil (NIST 2710 and NIST 2711), Mineral Soil and Till (TILL series), and
139 Sediments (NIST 2702 and CCRMP LKSD series) were used to test the extraction efficiency of
140 the methodology. The extraction efficiency testing was performed by an independent private lab,

141 using the same methodology used by the Health Canada lab (Niu et al., 2007b; Rasmussen et al.,
142 2007a). Certified water reference materials, NIST 1640, TMDA 64, and TM 28.3, were used for
143 assessing and monitoring instrument performance in the Health Canada lab.

144 *2.3. Gravimetric analysis*

145 Gravimetric analysis was performed inside Health Canada's Archimedes M3™ Buoyancy-
146 Corrected Gravimetric Analysis Facility, which was custom-designed to minimize weighing
147 errors (Rasmussen et al., 2006b). The Teflon filters were first pre-conditioned for at least 24-hr
148 inside a custom-designed chamber with automated controls to maintain environmental conditions
149 at a constant air temperature of 21 °C (± 0.5 °C) and constant relative humidity (RH) of 40 % (± 1
150 %). The possible static electricity interference was removed by passing each filter between two
151 polonium-210 strip deionizers placed side by side in the chamber. The filters were then weighed
152 using a Mettler UMX2 microbalance (readability of ± 0.1 μg).

153 Tared filters were loaded into pre-labeled polystyrene Petri dishes in Ottawa (Health Canada lab)
154 prior to transportation to the Windsor lab for assembly of the monitors for indoor, outdoor and
155 personal sampling in the WOEAS strategy. The filter samples were then returned to the same
156 holders after sampling and shipped back to Health Canada lab for post-weighing using the
157 procedures described earlier.

158 *2.4. Laboratory procedures*

159 The post-weighed Teflon filter samples were first analyzed by ED-XRF using an ED-XRF
160 spectrometer custom-built for US EPA by Lawrence Berkeley National Laboratory (Dzubay et al.,
161 1988) and were then digested using ultrasonication digestion in a HF-HNO₃ acid mixture
162 followed by ICP-MS analysis either at Health Canada or at a private laboratory (Alberta Research
163 Council, Vegreville, Alta; 24-hr duplicate samples). Both labs employed the same digestion

164 methods and the same ICP-MS instruments (Perkin Elmer ELAN DRC II) operated in dynamic
165 reaction cell mode for Cr and in standard mode for other elements. ED-XRF is a non-destructive
166 technique which allows subsequent ICP-MS analysis of the same filter samples, thus providing
167 data for direct comparison of the two methods.

168 Ultrasonication digestion in a strong HF-HNO₃ acid mixture was selected as the most appropriate
169 approach for handling large numbers of samples while at the same time minimizing the risk of
170 sample contamination (Niu et al., 2007b, 2008; Rasmussen et al., 2007a). The filters were
171 digested under clean laboratory conditions. A sample or field blank filter was placed into a 15 mL
172 digestion tube with 3 mL of HNO₃ (Seastar Chemical Inc.), 1 mL of HF (Seastar Chemical Inc.),
173 and 6 mL of deionized water (18 MΩ from Milli-Q Element water purification system. Millipore,
174 Billerica, MA) for digestion in a hot water bath at 60 °C for 6 days, with two 30 min ultrasonica-
175 tion intervals (Jalkanen et al., 1996). The digestion and analysis included three to six blank filters,
176 directly taken from the manufacturer's packaging, acting as "lab filter blanks". Ten laboratory
177 reagent blanks (consisting of reagents only) and three certified reference materials (CRMs) were
178 also included in each filter digestion and analytical batch for quality control. The lab filter blanks
179 and reagent blanks were used to assess contaminations from lab and reagent sources.

180 2.5. Assessment criteria

181 Two criteria were set in this study to further assess the overall performance of the air quality
182 monitoring procedures and to evaluate which elements are reportable. One is the "Pass-fail"
183 criterion with a cut-off value. For a given element, a "pass" was assigned when 70% and over of
184 the samples in a given set exceed the detection limit (DL), defined as three times the standard
185 deviation (3σ) of the measured concentrations of the eight to twelve procedural blanks, for either
186 ICP-MS or ED-XRF measurements. The "partially pass" and "fail" categories were defined as

187 when the passed percentage was larger than 20% but less than 70%, and equal to or less than
188 20%, respectively. Values for elements that “passed” or “partially passed” were considered
189 qualified for reporting, while values for failed elements were not recommended for further
190 analysis.

191 The second criterion is the relative percent difference (RPD) parameter used for evaluation of the
192 uncertainties associated with personal, indoor and outdoor monitoring duplicates (PM₁₀ or PM_{2.5})
193 samples. A pair of duplicate measurements was assigned a “pass” for the condition $RPD \leq 20\%$
194 (RPD criterion). The air concentration in $\mu\text{g m}^{-3}$ or ng m^{-3} was used for these assessments. Two
195 types of pairs, pairs from the same pumps and pairs from the different pumps were analyzed for
196 indoor and personal samples.

197 The analytes (PM₁₀, PM_{2.5}, or element) were grouped according to their duplicate pair
198 reproducibility into four categories: “Highly-Reliable”, “Reliable”, “Less-Reliable”, and
199 “Unreliable”. The percentage of duplicate pairs which pass the RPD criterion (P-RPD-Cri) was
200 used as the criterion. “Highly-Reliable” was defined as $P\text{-RPD-Cri} \geq 70\%$; “Reliable” was defined
201 as $50\% \leq P\text{-RPD-Cri} < 70\%$; “Less-Reliable” was defined as $20\% \leq P\text{-RPD-Cri} < 50\%$; and
202 “Unreliable” was defined as $P\text{-RPD-Cri} < 20\%$.

203 2.6. *Sample selection*

204 Low sample mass is a challenge for reliable metal analysis for not only ED-XRF but also for ICP-
205 MS, especially when low flow rates (1-5 L/min) and short sampling times (24-hr) are employed.
206 For all 2-week and 24-hr samples, filters with particle mass of at least 0.06 mg were selected for
207 elemental analysis. The 0.06 mg minimum cut-off for particle mass ensures reliable analysis
208 results for most elements using ICP-MS. As demonstrated in the pilot study (Rasmussen et al.,
209 2006a), samples below the minimum particle mass should not be included due to the ICP-MS

210 detection limits for key elements. For the 24-hr samples, only 9 out of 24 personal duplicate pairs
211 and 12 out of 24 indoor qualified for elemental determination by ICP-MS, while the remainder
212 had particle masses below the minimum mass requirement, which is typical for studies of this
213 type (Rasmussen et al., 2007a, 2008). For the two-week samples, all 9 outdoor duplicate pairs and
214 all 39 outdoor non-duplicate filter samples exceeded 0.06 mg.

215 **3. Results and discussion**

216 Numerous factors may cause variations and high uncertainties in the measurement of elements for
217 the PM collected in different environmental conditions (indoor, outdoor or personal). To focus on
218 the uncertainties, the two most commonly used instrumental approaches, ICP-MS and ED-XRF,
219 were employed for multi-element determination. Reliability of the elemental results was
220 investigated for two-week samples using inter-laboratory and inter-method comparisons, and for
221 24-hr samples using a duplicate study.

222 *3.1. Evaluation of extraction efficiency*

223 Efficient extraction (quantitative recovery) is essential when comparing indoor, outdoor and
224 personal environments, to eliminate bias introduced by different matrices and from the digestion
225 processes. It is also a precondition for inter-method comparisons between ED-XRF and ICP-MS
226 (Herner et al., 2006). Certified reference materials (CRMs) were used to test extraction efficiency
227 and to double check the analysis accuracy for ICP-MS determination (Figure 1).

228 A total of 31 elements were analysed by ICP-MS for a set of CRMs (ref. experimental section 2.2)
229 which represented a variety of environmental matrices (urban PM, indoor dust, coal fly ash, soil,
230 till, and sediment). Overall recoveries ranged from 73% to 127%, accounting for 98% of the total
231 measurement data. Only 3 exceptions were observed: Cr in Urban Particulate Matter NIST 1648,
232 yielding 30% recovery, Cd in Indoor Dust NIST 2583, yielding 63% recovery, and Zn in

233 geochemical soil TILL-4 yielding 138% recovery. The obtained 63% Cd recovery is well within
234 the wide acceptable certified value range of NIST 2583 (3.6 to 11.0 $\mu\text{g g}^{-1}$, corresponding to 49% -
235 150% acceptable recovery range) (NIST, 1996). Thus, the 63% recovery *reported* for Cd may not
236 necessarily reflect poor extraction efficiency but rather uncertainty in the original Cd
237 concentration. For Zn in Till-4, the high RSD and high reported recovery may be caused by
238 contamination during the analytical processes (Niu et al., 2007a; Rasmussen et al., 2007a). The
239 low recovery of Cr in NIST 1648 was expected as several previous studies have shown similarly
240 low recoveries (28% - 30%) for this CRM using the same digestion methods (Jalkanen et al.,
241 1996; Rasmussen et al., 2007a). The low recovery was due to the enrichment of refractory Cr
242 compounds in the NIST 1648 matrix (Lum et al., 1982), which are difficult to fully solubilize.

243 The graphs in Figure 1 show observed values (with Fe and Mn as examples) plotted against the
244 certified values for a wide range of CRMs. The observed results of Fe and Mn agree with the
245 certified values very well. Graphs for other elements (not presented here) show the same results,
246 indicating that the ICP-MS calibration and the overall digestion efficiencies are excellent for most
247 elements in most environmental sample matrices ($R^2 = 1$ and slope range from 0.9 to 1, Figure 1),
248 with the exception of Cr in NIST 1648 as discussed above. True total element techniques such as
249 ED-XRF, in which digestion is not needed, have an advantage in this regard. The experimental
250 results confirm that the acid digestion and ICP-MS determination approach employed in this study
251 was accurate and reliable. The present experiments confirm conclusions from previous digestion
252 protocols studies (Niu et al., 2007b; Rasmussen et al., 2007b) that strong acid digestion involving
253 HF is required to dissolve metals that are bound in stable materials such as silicates in PM.

254 3.2. 2-week outdoor $\text{PM}_{2.5}$ samples

255 The 2-week outdoor PM_{2.5} samples were collected from 39 different sites in summer 2005
256 throughout the city of Windsor. Elemental concentrations of these 2-week PM_{2.5} samples are
257 determined using two different analytical approaches: first by ED-XRF (US-EPA lab) and then
258 followed by HF-HNO₃ digestion/ICP-MS (Health Canada lab). Over 20 elements were analyzed
259 by both techniques. Not all of these elemental measurements from the 39 sampling sites pass the
260 detection limits (DLs) of both ED-XRF and ICP-MS. Results shown in Table 2 indicate that Fe,
261 Zn, Mn, Cu, Pb, and V are the top six elements with highest concentrations. Correspondingly,
262 they also show the highest DL-passing rate (nearly 100% for all of them except 80% for V and
263 97% for Cu for ED-XRF analysis, Table 2). Among these elements, the concentration ranges of
264 Fe, Zn, Mn, and Cu across the different sampling sites are large, indicating their relatively large
265 variations in spatial distribution. On the other hand, spatial variation of Pb and V is relatively
266 small as evidenced by their narrow concentration ranges (Table 2).

267 Results show that the maximum PM_{2.5} concentration in the present Windsor data set (23.3 µg m⁻³)
268 was comparable to the maximum PM_{2.5} value of 23.2 µg m⁻³ from a previous study of 22 Ottawa
269 homes (Rasmussen et al., 2006a), though the median value of 19.7 µg m⁻³ in Windsor was more
270 than two times the median value (9.0 µg m⁻³) in Ottawa. For trace metals (e.g. Cu, Pb, and Ni),
271 their median concentrations were similar in the two cities. All their maximum concentrations were
272 much lower than occupational exposure limits (NIOSH, 2003) in both cities.

273 Table 2 shows that Fe, Zn, Mn, Cu, Pb and V pass the DL criterion for both ICP-MS and ED-
274 XRF. Other elements such as Cr, As, Ni, and Sr also exhibited high DL-passing rates (from 92%
275 to 100%) for ICP-MS but not for ED-XRF (from 33% to 69%) for these elements due to their low
276 air concentrations ($C_{\text{median}} < 1.3 \text{ ng m}^{-3}$). Such low air concentrations posed a great challenge for
277 accurately quantifying metals in PM and the subsequent risk assessment. The key concern is
278 sample contamination. Any contamination may cause over-quantification errors or introduce

279 interferences leading to unacceptable analytical uncertainties. Great care must be taken to avoid or
280 minimize sources of contamination both in the field and in the laboratory.

281 Generally, the elemental concentration results (range, median, geometric mean and arithmetic
282 mean) from the ICP-MS and ED-XRF compare well, especially for high concentration elements
283 (Table 2). The direct comparison of the element analysis of these two methods (Figure 2) yielded
284 very good correlations ($R^2 \geq 0.7$) for elements (including Fe, Mn, Zn, Pb and Cu, not all shown in
285 Figure 2) having both high DL-passing rates and concentrations that were above 2 ng m^{-3} (Table
286 2). Correlations were weakened or lost for elements with either very low concentrations ($<2 \text{ ng m}^{-3}$)
287 or very low DL-passing rates using ED-XRF, such as V, Cr, Ti, Ni, As, and Sr.

288 A two-tail paired *t*-test was used to determine if there was a significant difference when
289 comparing individual results on the same sample. No significant difference was found for Zn, Fe,
290 and Cu ($n = 39$; $p > 0.08$). However, there were significant differences for Mn, Pb and V. The
291 difference for V was expected due to its both low ED-XRF DL-passing rate and R^2 (0.47) values.
292 The differences for Mn and Pb were probably due to the relative higher values from ED-XRF
293 measurements for these two metals as indicated by their relative high slopes which from 1.15 to
294 1.19. Such slope values and the highly correlated characteristics (R^2 are 0.73 and 0.95 for Pb and
295 Mn, respectively) indicate bias between ICP-MS and ED-XRF for detecting these two metals.
296 These variances were, however, considered acceptable given the fundamental differences of the
297 two techniques.

298 3.3. 24-hour outdoor $PM_{2.5}$ samples

299 More challenges occurred for element determinations of 24-hr low-flow filter samples ($n=9$).
300 Compared to the 2-week samples, the DL-passing rates of ED-XRF show significant decreases for
301 Cu, Pb, V, Cr, and As, from 97% to 61%, 100% to 28%, 80% to 6%, 33% to 6% and 69% to 0%,

302 respectively (Tables 2 and 3), due to the limited particle mass collected in this short (24-hr) time
303 period. This led to the weak or complete lack of correlations of such elements between ICP-MS
304 and ED-XRF. Elements with high concentrations, such as Fe, Zn and Mn, however, maintained
305 high DL-passing rates (nearly all 100%) for both ICP-MS and ED-XRF (Table 3). These elements
306 were highly correlated (Figure 3, R^2 around 1.1, slope >0.8), even in 24-hr sampling cases,
307 indicating again the good agreement between ICP-MS and ED-XRF measurements provided that
308 minimum requirements of particle mass and metal concentration are met for both instruments.

309 The decrease in the number of species that are well correlated between ICP-MS and ED-XRF for
310 24-hr sampling filters emphasizes the challenge of low mass loadings on element determination
311 using ED-XRF and ICP-MS. Obviously, decrease of the particle mass leads to the increase of the
312 uncertainty of the determination. However, the cause of uncertainty for ED-XRF and for ICP-MS
313 may be different. The higher detection limit plus the possible heterogeneity of the particle films
314 on the filters at low particle concentrations may be the main contributions to the uncertainties in
315 ED-XRF as indicated by the low DL-passing rates for most elements in Table 3. However,
316 depending on elements, these two uncertainty factors in ED-XRF may have a limited effect on
317 ICP-MS detection. Sample contamination plays an important role in ICP-MS variability (see
318 discussion below). Compared with ED-XRF where analysis is simple and non-destructive, the
319 long and complicated pre-treatment and digestion processes associated with ICP-MS require extra
320 care to avoid contamination leading to unwanted variability.

321 *3.4. 24-hour duplicate study*

322 To evaluate uncertainty associated with personal, indoor and outdoor monitoring, duplicate
323 samples (PM_{10} or $PM_{2.5}$) were evaluated using the relative percent difference (RPD) criterion
324 described in experimental section 2.5. A pair of duplicate measurements was assigned a “pass”

325 when $RPD \leq 20\%$. The percentages of the duplicate pairs which pass the RPD criterion (P-RPD-
326 Cri) were used to evaluate the sampling quality (ref. experimental section 2.5).

327 The PM analysis results for indoor, outdoor, and personal duplicate samples were all Highly-
328 Reliable with P-RPD-Cri from 92 % to 100%. The results for pairs using the same pumps and for
329 pairs using different pumps for indoor (92% vs 92%) and personal samples (92% vs 96%)
330 generally showed no significant difference.

331 Elemental analysis results shown in Figures 4 and 5 indicate that the degree of variation was
332 element specific. For outdoor samples, the Highly-Reliable elements as evaluated by ED-XRF
333 (Figure 4) were S, Ca, Fe, Mn, and Zn with P-RPD-Cri $\geq 70\%$. Reliable elements were Br and K
334 (may also include Si and Pb) with P-RPD-Cri around 50% or higher. Note that the Highly-
335 Reliable and Reliable elements are limited in number due to the low mass loading on the filters,
336 causing many concentrations to fall below the detection limits of ED-XRF for these elements.

337 For indoor and personal duplicate pairs assessed by ICP-MS, the results showed that the Highly-
338 Reliable and Reliable category elements were Li, Na, K, Ca, Al, Si, Mn, Fe, Co, Cu, Pb, As, V,
339 Sb, Sn, Sr, Mo, Ag, Ti, Mg, Th, Tl, and U (Figure 5). Calculations of variability for pairs from the
340 same pump, or from two separate pumps for indoor pairs exhibit no significant difference (Figures
341 5a and 5b): Highly-Reliable, and Reliable + Less-Reliable element numbers are nearly the same.
342 For personal sample pairs, however, more elements fell into the category of Highly-Reliable and
343 fewer fell into the categories of Reliable and Less-Reliable when using different pumps (Figure
344 5c) as compared to the pairs using the same pumps (Figure 5d). These results suggest that pumps
345 may have some effect on variability in personal sampling compared to stationary sampling. Note
346 that such pump-related differences were not observed for indoor sampling, indicating the
347 differences in personal sampling may be caused by individual participant behaviour, as reported

348 in previous work (Williams et al., 2003) showing that there is a statistically significant difference
349 in duplicate personal sample PM_{2.5} mass concentrations relative to the handedness of the person.
350 However, in this study, the difference between the same and the different pumps was less
351 significant if the total number of Highly-Reliable plus Reliable elements were considered together
352 in personal sampling (Figures 5c and 5d).

353 Comparing Figures 5a and 5b with Figures 5c and 5d, significant differences between indoor and
354 personal sampling were observed. It appears that indoor has more Highly-Reliable + Reliable (and
355 therefore fewer Less-Reliable + Unreliable) elements than personal sampling. This phenomenon
356 might imply some individual behavioral and/or environmental effect on personal airborne PM
357 sampling. The sampling environments continuously change with a participant's movement from
358 one place to another, which might be one of the causes of the increased variability in personal
359 sampling as compared with the stationary indoor sampling. The mechanism is unclear and
360 requires further investigation.

361 *3.5. Uncertainty contribution to PM and element assessment*

362 The comparison results of the RPD variations for PM and metals (in ICP-MS data) shown in
363 Figure 6 indicated that PM variations assessed for indoor and personal duplicate pairs were
364 consistently very low (RPD < 10%). Elemental variations were generally higher than that of PM,
365 and were strongly element-dependent. Some of them yielded large variations that exceed the RPD
366 criterion (RPD > 20%). Such RPD differences between PM and elemental assessments suggest
367 that significant sources of metal contamination, in addition to physical sampling variability, might
368 contribute to the overall uncertainty for many metal exposure assessments.

369 Three certified reference materials (TM 28.3, TMDA-64, and NIST 1640) are trace metals in
370 water which were used to test ICP-MS instrument performance and its contribution to overall

371 variability. Table 4 summarizes the results which show very low uncertainties (RPD < 1%) in
372 most cases. This result eliminates the instrument performance reproducibility as a significant
373 contributor to the elemental analysis variations. Blank analysis results showed that contamination
374 was one of the main causes for variations in metal determination using ICP-MS. The overall
375 contamination contributed up to 20 to 75 ng filter⁻¹ for some elements such as Cu, Zn, Pb, and Sr.
376 The sources of contamination can vary depending on the element, and can arise at every stage of
377 handling, transportation, and laboratory processes. For example, the main contamination of Pb
378 came from field processes (including field sampling, handling, and transportation) accounting for
379 76% of its total blanks (Figure 7). For Cu and Zn, the main contamination was from lab processes
380 (including filter preparation, weighing, digestion, and determination processes) contributing 93%
381 to 97% of their overall blanks in this study. The contribution of contamination for Sr was almost
382 equal from each of the handling and treatment processes (Figure 7). Thus, data reliability must be
383 assessed separately for each element. Previous testing (Rasmussen et al., 2006a) indicated that
384 metal contamination is introduced from unknown sources during all sample handling in
385 cumulative amounts that may exceed the contribution from the particles themselves if appropriate
386 precautions were not taken. Omitting unnecessary handling procedures to minimize sample
387 contamination improves the analysis methodology and lowers the detection limit significantly
388 (Niu et al., 2007a; Rasmussen et al., 2007a). Similar concerns were raised by Graney (Graney et
389 al., 2004), who observed that additional contamination arises when filters are transferred through
390 multiple (non-destructive) instrumental methods of analysis prior to the final acid digestion.

391 There are two more challenging factors that have significant effect on metal measurement
392 uncertainties: the very low particle mass for 24-hr low flow sampling filters and the very low
393 concentrations of metals in airborne particles. Such low particle mass and low metal
394 concentrations require sensitive instrumentation with very low detection limit to ensure reliable

395 and accurate analysis. Adequate sensitivity is achieved for many metals using ICP-MS but
396 contamination can also easily and extensively exceed such low detection limits. Thus, at present,
397 the analytical capabilities have exceeded the capabilities to control contamination levels. More
398 challenges therefore arise for contamination control at each stage of analysis: from sample
399 handling to filter weighing, exposure to the lab environment, digestion, water, and reagents. Even
400 the pipettes themselves can contribute 1.6 ppb Fe, 2.0 ppb Co, 5.4 ppb Pb, 6.4 ppb Al, 9 ppb Zn,
401 18.8 ppb Ca and 19.1 ppb Na, respectively (PerkinElmer, 2003). Every effort has to be made to
402 minimize contamination of filters through all stages of sampling and determination. Every
403 unnecessary handling or pretreatment step should be eliminated to further improve analysis
404 methodology and lower the measurement uncertainties.

405 **4. Conclusions**

406 Results in this study indicate that to benefit from the improved sensitivity and lower detection
407 limits that are associated with ICP-MS, rigorous operations are required to eliminate all the
408 possible sources of contamination. Both the inter-laboratory, inter-method comparisons, and
409 duplicate sample analysis will help to evaluate the data reliability and to identify and quantify the
410 possible sources of variations during sampling, handling and processing.

411 PM assessments in collocated duplicates revealed that the indoor and personal sampling
412 procedures for PM₁₀ samples, and the outdoor sampling for PM_{2.5} samples, were reliable, with ≥
413 92% to 100% duplicates passing the RPD ≤20% criterion. Direct comparison of the two
414 fundamentally different techniques, ICP-MS and ED-XRF, resulted in good correlations for both
415 24-hr and 2-week sampling filter samples for elements that were above detection limits for both
416 instruments. Note that bias was also observed for certain elements, highlighting that correction
417 factors may need to be applied in such circumstances to ensure data equivalence between ICP-MS

418 and ED-XRF, as in the case for PM monitoring using different science-based techniques
419 (Butterfield and Quincey, 2007)

420 Total sample volume is one of the key factors influencing both the uncertainty of PM and
421 elemental assessments and correlations between ICP-MS and ED-XRF results. Larger sample
422 volume resulting from longer sampling time usually ensures better elemental correlations and
423 lower uncertainties. However, extended sampling times yield decreased temporal resolution and
424 less specificity about sources. Therefore, a compromise must be made between uncertainty and
425 temporal resolution/specificity of the source apportionment.

426 Uncertainty for element assessment mainly comes from contamination rather than sampling
427 strategy. In addition, higher uncertainty associated with the shorter sampling period (24-hr) is the
428 serious challenge in obtaining reliable element data due to the very small particle mass collected
429 with low-flow pumps, especially for personal monitoring in which very low-flow rates must be
430 used to minimize both pump weight and battery drain.

431 Contamination, which varies from element to element, can arise from every stage of handling,
432 transportation, and laboratory processing. Thus, the acceptability of elemental concentrations
433 must be assessed on an element by element basis, for each individual sampling situation. Extreme
434 caution must be exercised to avoid contamination of filters during all stages of sampling and
435 determination processes. Minimal pre-treatment of the filter samples should be employed to
436 eliminate any unnecessary steps that may introduce contamination, and consequently to further
437 decrease measurement uncertainty and improve analysis accuracy and precision.

438 Variability of duplicates sharing the same pump was comparable to variability of duplicates from
439 different pumps in the same location, indicating that pumping is not the main source of duplicate
440 variability. There was no significant difference in reproducibility whether pairs are from the same

441 pump or from different pumps for PM assessment in both indoor and personal monitoring, and for
442 elemental assessment in the indoor environment. Though slight differences occur in elemental
443 assessment for personal monitoring, the differences were not statistically significant. Uncertainty
444 in personal sampling was increased as compared with the indoor sampling. Environmental and/or
445 individual participant behavioral reasons may account for such uncertainty differences amongst
446 environments.

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Legends

Table 1. Sampling scheme.

Table 2. Comparison of ICP-MS and ED-XRF results for 2-week outdoor PM_{2.5} filter samples (n= 39).

Table 3. ICP-MS and ED-XRF results for 24-hr outdoor PM_{2.5} filter samples (n=9).

Table 4. Elemental relative percent difference (RPD) values analysed by ICP-MS for Certified Reference Materials.

Figure 1. Quality assurance results for ICP-MS analysis using Certified Reference Materials. Graphs compare certified and observed values for a variety of matrix types with Fe and Mn as examples.

Figure 2. Direct comparison of ICP-MS and ED-XRF for elemental analysis of the 2-week outdoor PM_{2.5} filter samples (with Fe and Zn as examples).

Figure 3. Direct comparison of ICP-MS and ED-XRF for elemental analysis of the 24-hr outdoor PM_{2.5} filter samples (with Fe and Zn as examples).

Figure 4. Elemental analysis results using ED-XRF for outdoor co-located duplicate filters. P-RPD-Cri: The percentages of the duplicate pairs which pass the RPD criterion. ■ - 70% or more pass; ☒ - 50% to 69% pass; ▨ - 20% to 49% pass; and □ - less than 20% pass. See text for details.

Figure 5. Elemental analysis results using ICP-MS for indoor and personal co-located duplicate filters. P-RPD-Cri: The percentages of the duplicate pairs which pass the RPD criterion. ■ - 70% or more pass; ☒ - 50% to 69% pass; ▨ - 20% to 49% pass; and □ - less than 20% pass. See text for details.

Figure 6. Comparison of PM and elemental relative percent difference (RPD) variations for indoor (a) and personal (b) co-located duplicate samples. Elemental data are from ICP-MS.

Figure 7. Results for elemental blank analysis by ICP-MS. Pie diagrams show the proportional contribution of different sources of contamination to the blanks.

Table 1. Sampling scheme

Sample type	Sampling time	Collecting environment	Sample type	Sample numbers
Non-duplicates	2 weeks	Outdoor	PM _{2.5}	39
Co-located duplicates	2 weeks	Outdoor	PM _{2.5}	9
	24 hours	Outdoor	PM _{2.5}	18
	24 hours	Indoor	PM ₁₀	48
	24 hours	Personal	PM ₁₀	48
Field blanks	2 weeks	Outdoor		3
	24 hours	Outdoor		3
	24 hours	Indoor		3
	24 hours	Personal		3
Lab filter blanks				3 in one batch analysis
Gravimetric blanks				1 for each 10 samples
Reagent blanks				8 to 12 in one batch analysis
NIST CRMs				3 for each CRM in one batch analysis

Table 2. Comparison of ICP-MS and ED-XRF results for 2-week outdoor PM_{2.5} filter samples (n= 39).

Elements	Method	Concentration Range (ng m ⁻³)	Median (ng m ⁻³)	Geomean (± sd) (ng m ⁻³)	Mean (± sd) (ng m ⁻³)	Sample > DL (%)
Mass		13221.4 - 23294.6	19685.4	19604.4 ± 1732.8	19684.4 ± 1732.8	100
Fe	ICP-MS	49.3 - 217.0	115.8	115.3 ± 37.9	121.0 ± 37.9	100
	ED-XRF	67.1 - 242.9	110.9	117.6 ± 38.3	122.7 ± 38.3	100
Zn	ICP-MS	13.8 - 57.8	26.2	26.6 ± 8.9	27.9 ± 8.9	100
	ED-XRF	16.7 - 57.7	26.6	27.8 ± 9.5	29.1 ± 9.5	100
Mn	ICP-MS	2.4 - 10.2	3.8	4.0 ± 1.5	4.2 ± 1.5	100
	ED-XRF	2.5 - 12.1	4.6	4.5 ± 1.7	4.8 ± 1.7	100
Cu	ICP-MS	0.9 - 10.2	2.1	2.4 ± 2.0	2.8 ± 2.0	100
	ED-XRF	<DL - 11.5	2.7	2.7 ± 1.6	3.0 ± 1.6	97
Pb	ICP-MS	2.3 - 5.9	3.4	3.5 ± 0.8	3.6 ± 0.8	100
	ED-XRF	2.4 - 7.9	4.1	4.0 ± 1.2	4.2 ± 1.2	100
V	ICP-MS	0.7 - 2.0	1.4	1.4 ± 0.3	1.4 ± 0.3	100
	ED-XRF	<DL - 3.2	1.7	1.4 ± 0.6	1.6 ± 0.6	80
Ti	ICP-MS	<DL - 17.2	- ^a	-	-	18
	ED-XRF	<DL - 5.6	2.8	-	-	59
Ni	ICP-MS	<DL - 2.9	1.3	0.9 ± 0.7	1.4 ± 0.6	92
	ED-XRF	<DL - 1.8	1.0	-	-	59
As	ICP-MS	0.2 - 2.4	0.9	0.7 ± 0.7	1.0 ± 0.7	100
	ED-XRF	<DL - 2.1	1.3	-	-	69
Cr	ICP-MS	0.1 - 1.0	0.6	0.5 ± 0.2	0.6 ± 0.2	100
	ED-XRF	<DL - 1.1	-	-	-	33
Sr	ICP-MS	<DL - 1.6	0.6	0.4 ± 0.4	0.7 ± 0.4	92
	ED-XRF	<DL - 1.5	0.8	-	-	56

DL = detection limit. ^a Value not calculated due to large % samples below DL.

Table 3. ICP-MS and ED-XRF results for 24-hr outdoor PM_{2.5} filter samples (n = 9).

Elements	Method	Concentration Range (ng m ⁻³)	Median (ng m ⁻³)	Geomean (ng m ⁻³)	Mean (± sd) (ng m ⁻³)	Sample >DL (%)
Mass		16717.2 - 40597.2	21312.2	22873.0	24030.3 ± 8507.9	100
Fe	ICP-MS	85.3 - 382.3	261.1	219.5	239.7 ± 96.4	100
	ED-XRF	110.6 - 432.8	242.2	238.9	259.3 ± 103.1	100
Zn	ICP-MS	14.5 - 57.2	48.1	40.3	43.4 ± 14.4	100
	ED-XRF	19.3 - 76.9	55.7	49.5	52.5 ± 16.0	100
Mn	ICP-MS	3.7 - 19.1	11.4	10.0	11.3 ± 5.6	100
	ED-XRF	<DL - 28.7	12.6	11.5	13.5 ± 7.7	89
Cu	ICP-MS	<DL - 28.1	2.2	1.8	5.5 ± 9.0	89
	ED-XRF	<DL - 21.1	6.9	- ^a	-	61
Pb	ICP-MS	3.1 - 13.1	6.6	6.7	7.2 ± 2.9	100
	ED-XRF	<DL - 14.4	-	-	-	28
V	ICP-MS	0.45 - 3.1	1.2	1.1	1.3 ± 0.9	100
	ED-XRF	<DL - 6.6	-	-	-	6
As	ICP-MS	<DL - 1.7	-	-	-	0
	ED-XRF	<DL - 2.8	-	-	-	0
Cr	ICP-MS	<DL - 1.2	-	-	-	44
	ED-XRF	<DL - 8.0	-	-	-	6

DL = detection limit. ^a Value not calculated due to large % samples below DL.

Table 4. Elemental Relative Percent Difference (RPD) values analysed by ICP-MS for Certified Reference Materials *

Analyte	V	Fe	Mn	Cu	Zn	Pb
TM28.3	0.5 (0.4)	3.2 (2.0)	1.4 (1.0)	0.8 (0.5)	1.2 (0.7)	0.3 (0.3)
TMDA-64	1.1 (0.7)	0.6 (0.3)	0.6 (0.3)	1.1 (0.7)	0.4 (0.2)	0.6 (0.3)
NIST 1640	0.5 (0.4)	1.4 (0.6)	0.6 (0.3)	1.4 (1.0)	0.7 (0.3)	0.0 (0.0)

* Values are the average of three analysis with standard deviation in bracket. TM28.3 and TMDA 64 are trace metals in filtered and diluted Lake Ontario waters from the National Water Research Institute. NIST 1640 is trace metals in natural fresh water from the National Institute of Standards & Technology.

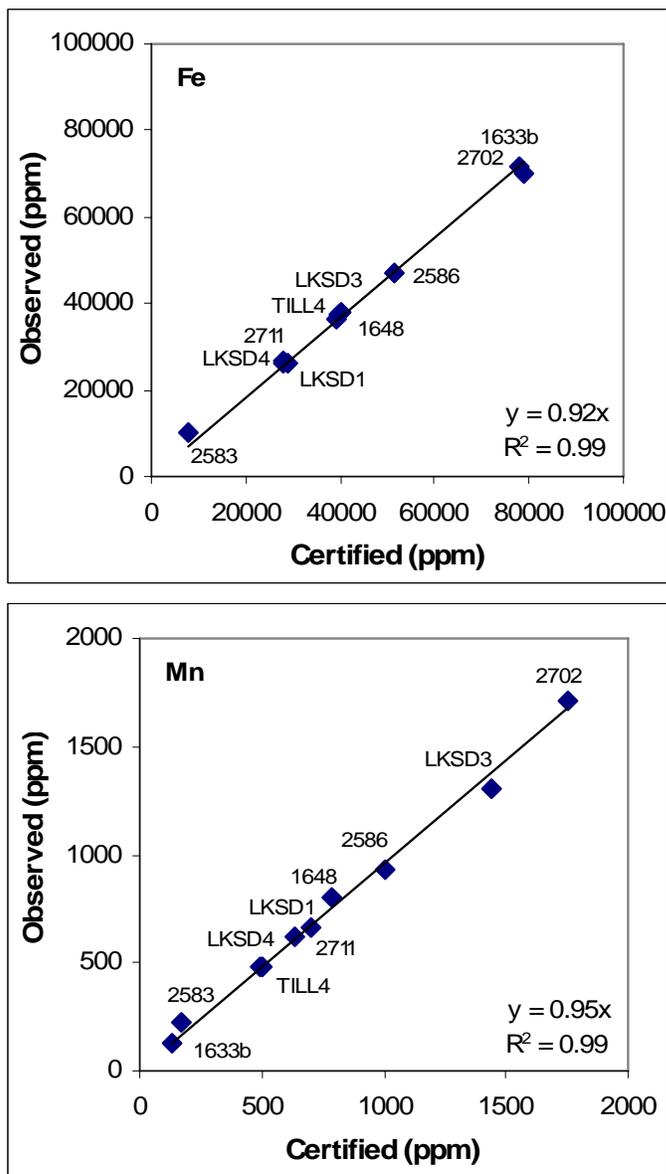


Figure 1. Quality assurance results for ICP-MS analysis using Certified Reference Materials. Graphs compare certified and observed values for a variety of matrix types with Fe and Mn as examples.

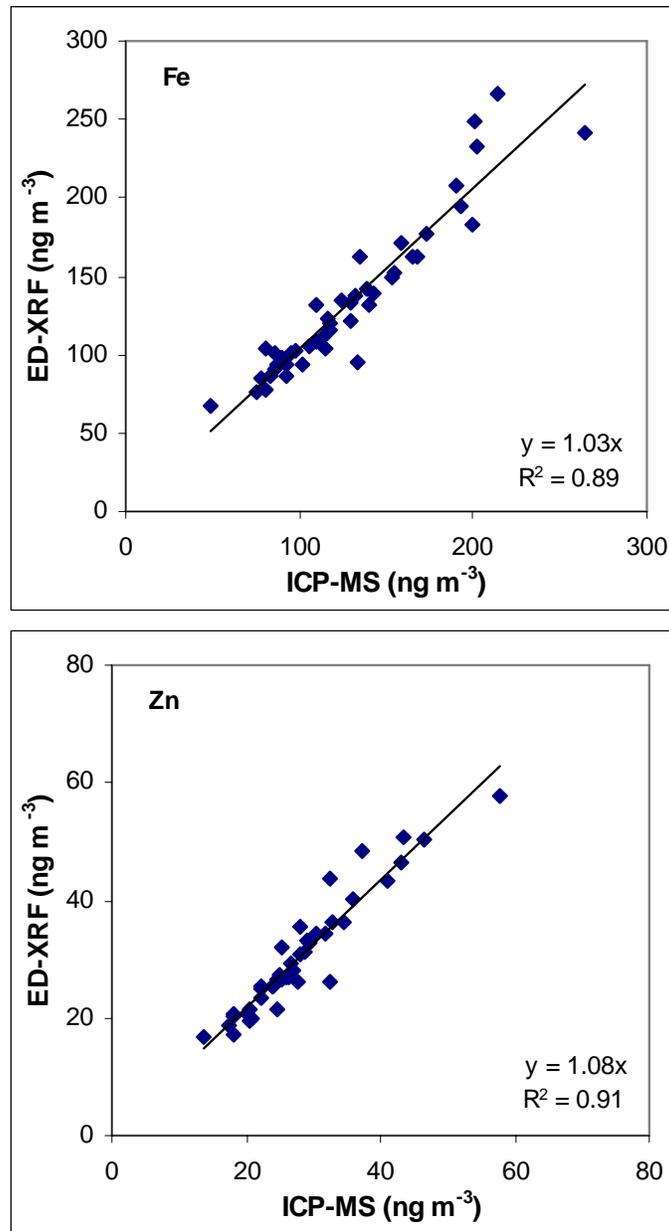


Figure 2. Direct comparison of ICP-MS and ED-XRF for element analysis of the 2-week outdoor PM_{2.5} filter samples (with Fe and Zn as examples).

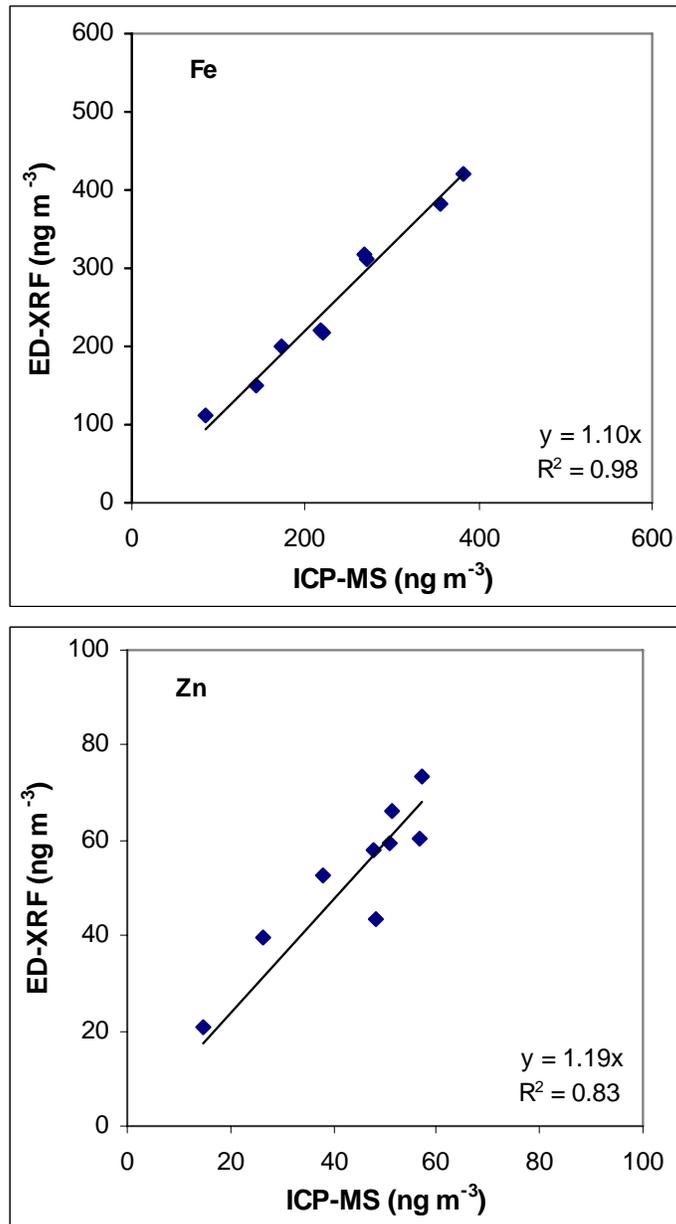


Figure 3. Direct comparison of ICP-MS and ED-XRF for elemental analysis of the 24-hr outdoor $\text{PM}_{2.5}$ filter samples (with Fe and Zn as examples).

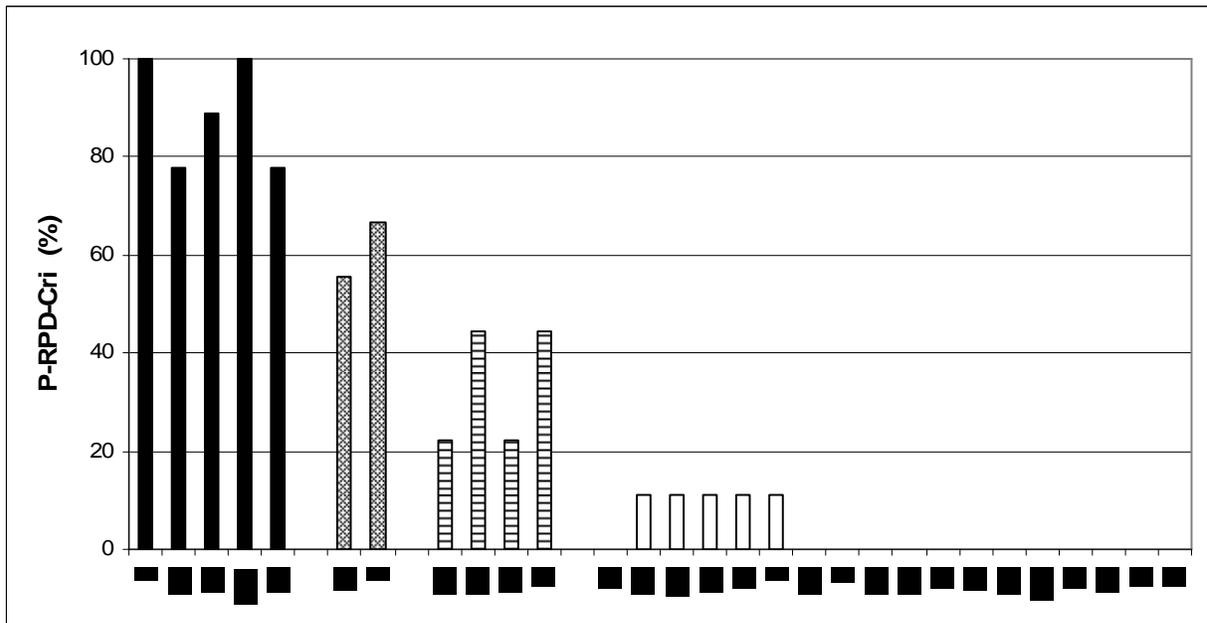


Figure 4. Elemental analysis results using ED-XRF for outdoor co-located duplicate filters. P-RPD-Cri: The percentages of the duplicate pairs which pass the RPD criterion. ■ - 70% or more pass; ▣ - 50% to 69% pass; ▤ - 20% to 49% pass; and □ - less than 20 % pass. See text for details.

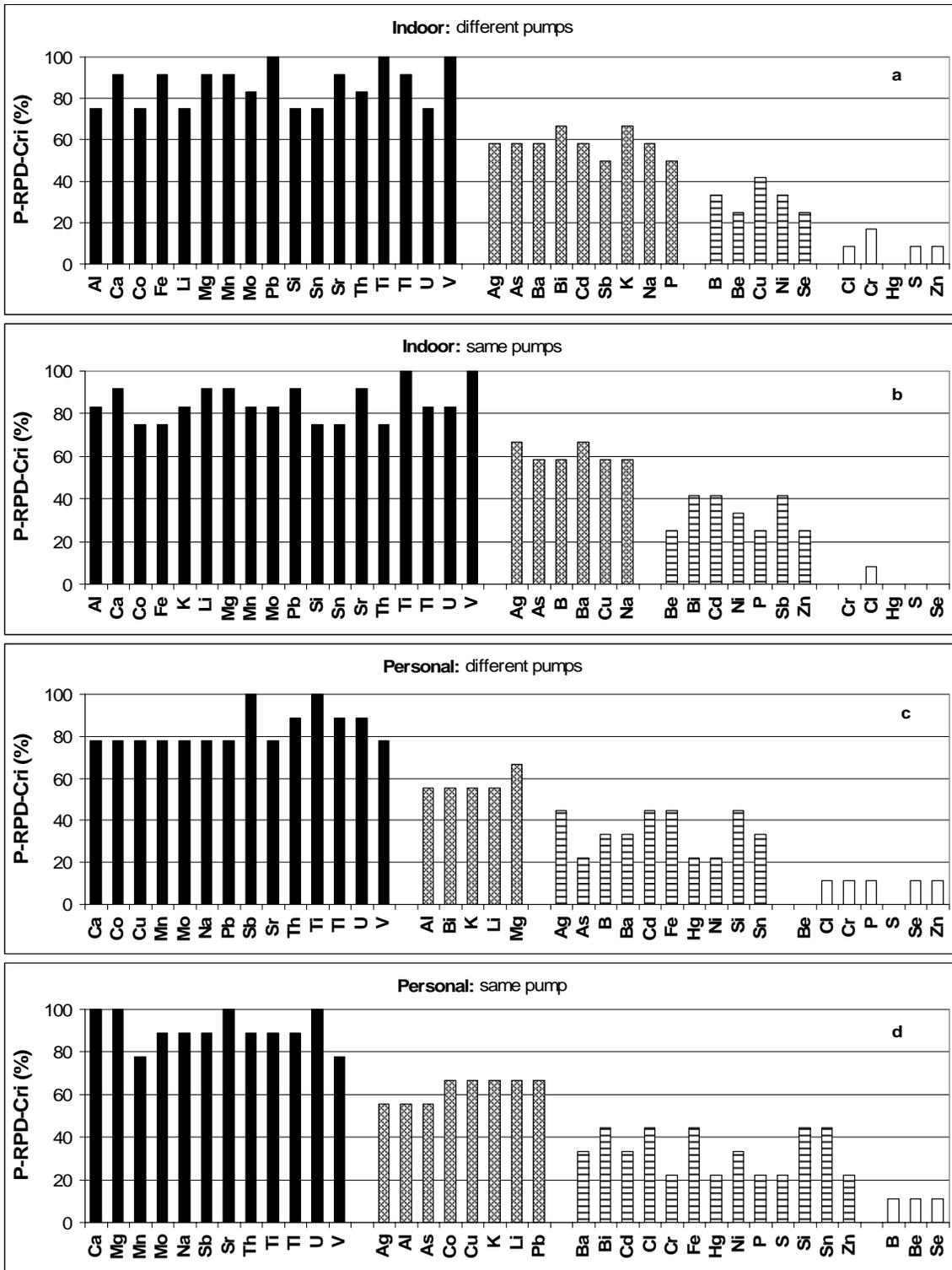


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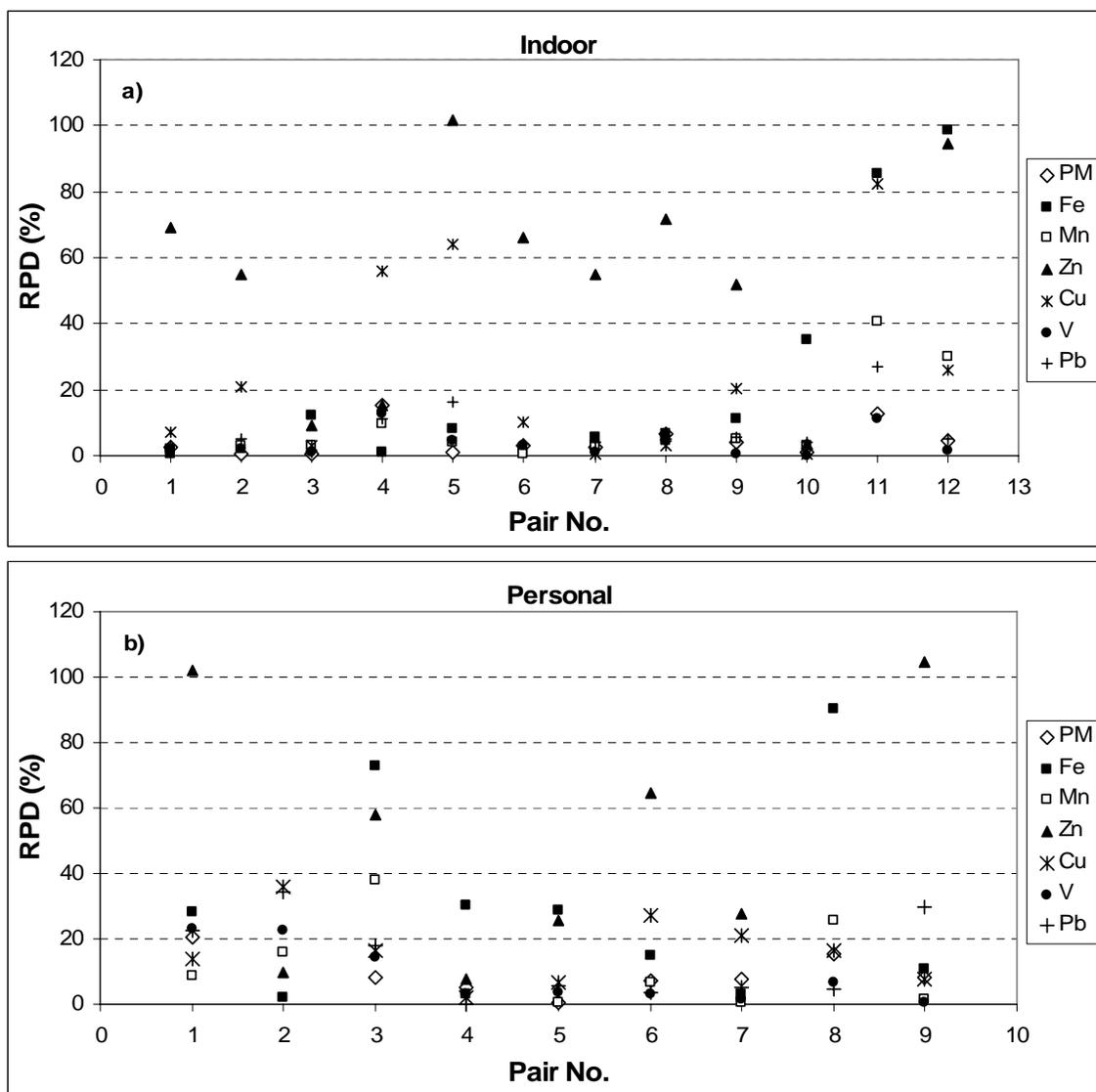


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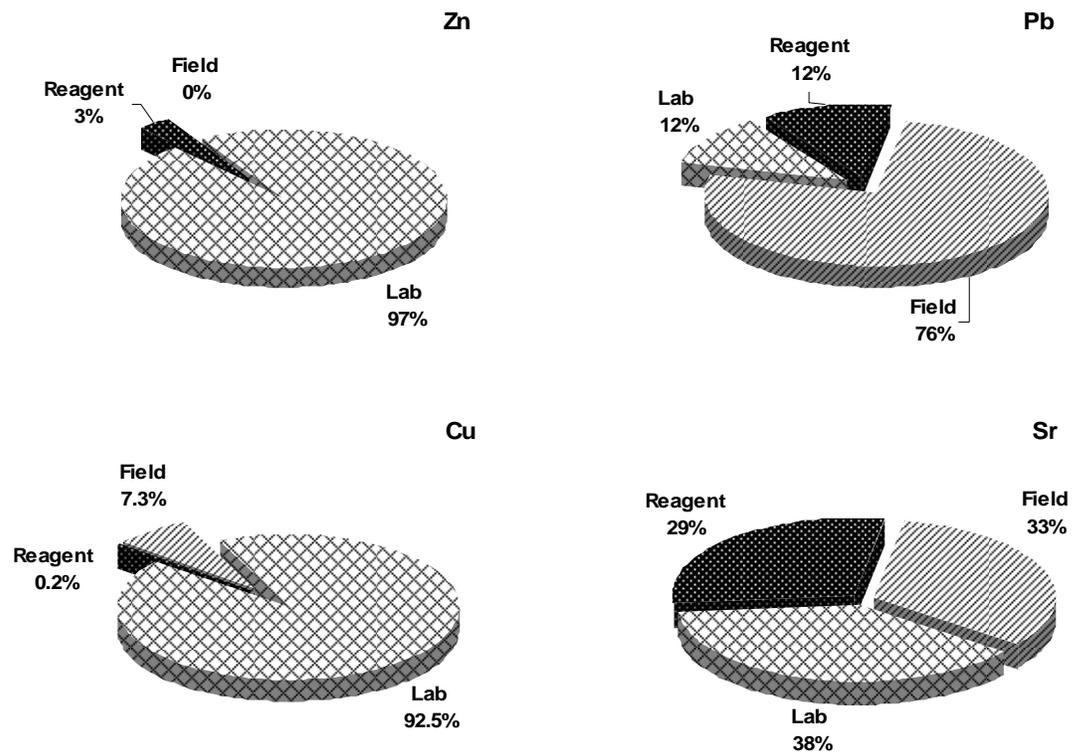


Figure 7. Results for elemental blank analysis by ICP-MS. Pie diagrams show the proportional contribution of different sources of contamination to the blanks.