

1 **Oxidative potential and chemical composition of PM_{2.5} in office buildings across Europe –**

2 **The OFFICAIR study**

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32 **Abstract**

33

34 In the OFFICAIR project, indoor and outdoor PM_{2.5} samples were collected in office buildings
35 across Europe in two sampling campaigns (summer and winter). The ability of the particles to
36 deplete physiologically relevant antioxidants (ascorbic acid (AA), reduced glutathione (GSH)) in
37 a synthetic respiratory tract lining fluid, i.e., oxidative potential (OP), was assessed. Furthermore,
38 the link between particulate OP and the concentration of the PM constituents was investigated.
39 The mean indoor PM_{2.5} mass concentration values were substantially lower than the related
40 outdoor values with a mean indoor/outdoor PM_{2.5} mass concentration ratio of 0.62 and 0.61 for
41 the summer and winter campaigns respectively. The OP of PM_{2.5} varied markedly across Europe
42 with the highest outdoor OP^{AA} m⁻³ and OP^{GSH} m⁻³ (% antioxidant depletion/m³ air) values
43 obtained for Hungary, while PM_{2.5} collected in Finland exhibited the lowest values. Seasonal
44 variation could be observed for both indoor and outdoor OP^{AA} m⁻³ and OP^{GSH} m⁻³ with higher
45 mean values during winter. The indoor/outdoor OP^{AA} m⁻³ and OP^{GSH} m⁻³ ratios were less than
46 one with 4 and 17 exceptions out of the 40 cases respectively. These results indicate that indoor
47 air is generally less oxidatively challenging than outdoors. Correlation analysis revealed that trace
48 elements play an important role in determining OP, in particular, the Cu content. Indoor air
49 chemistry might affect OP since weaker correlations were obtained for indoor PM_{2.5}. Our
50 findings also suggest that office workers may be exposed to health relevant PM constituents to a
51 different extent within the same building.

52

53 **Keywords:** environmental health; indoor air quality; occupational exposure; office building;
54 oxidative potential; PM_{2.5}

55

56 **1. Introduction**

57
58 Numerous epidemiological and toxicological studies have shown a relationship between ambient
59 particulate matter (PM) exposure and adverse health effects in humans (Brook et al., 2010; Hoek
60 et al., 2002; Laden et al., 2000; Schwartz et al., 2002). Different pathophysiological mechanisms
61 have been proposed to explain PM's contribution to respiratory and cardiovascular diseases;
62 however, there are still remaining questions to be answered. Many of the air pollution related
63 health outcomes are thought to derive from oxidative stress initiated by certain gaseous air
64 pollutants (i.e., nitrogen dioxide, ozone) or PM constituents in the lung (Ayres et al., 2008; Kelly,
65 2003; Nel, 2005). The pulmonary epithelial cells are protected against undue oxidation by the
66 respiratory tract lining fluid (RTLFL) which contains low-molecular weight antioxidants (i.e.,
67 reduced glutathione, ascorbate, urate) and antioxidant enzymes. Either the increased exposure to
68 oxidants or the presence of decreased antioxidant defenses could lead to oxidative stress which in
69 turn can activate a number of redox sensitive signaling pathways (Anseth et al., 2005; Kelly,
70 2003; Kelly and Fussell, 2012). However, the identification of the oxidatively active components
71 of PM is still a challenging task since particles vary in size, mass, number, shape, aggregation
72 status, surface area as well as chemical composition.

73 Oxidative potential (OP) is a novel metric which is defined as a measure of the capacity of PM to
74 oxidize target compounds. *In vitro* acellular methods based on different principles (i.e.,
75 antioxidant depletion, hydroxyl radical formation in the presence of H₂O₂, consumption of
76 dithiotreitol, fluorescent probes) have been developed and used for the assessment of the OP of
77 aerosol particles. Previous studies suggest that various chemical compounds such as certain
78 transition metals (e.g., Fe, Cu, Cr), aromatic organic compounds (e.g., quinones) and some major
79 PM constituents (e.g., humic-like substances) contribute to particulate OP (e.g., Godri et al.,
80 2010; Roginsky et al., 1999; Szigeti et al., 2015; Verma et al., 2012). The importance of the
81 water-soluble part of the trace elements has also been proposed since higher correlations may
82 occur between them and the OP metrics compared to the total trace element concentrations
83 (Szigeti et al., 2015). Although, several studies have linked increased PM_{2.5} mass concentration to
84 adverse health effects, the use of OP in epidemiology has also been suggested as a promising
85 metric since it may better represent the health impact of the aerosol particles (Borm et al. 2007;

86 Boogaard et al. 2012; Szigeti et al., 2015; Yang et al., 2015). However, there is still no consensus
87 about which OP metrics are the most appropriate to predict PM-related health effects.

88 Outdoor locations (i.e., urban, rural, industrial sites) are well characterized (in terms of PM mass
89 concentration and chemical composition) over almost the entire world due to the existing
90 regulations on the mass concentration of PM₁₀ and PM_{2.5}; however, less information is available
91 about PM in indoor microenvironments, particularly in offices (Chatoutsidou et al., 2015;
92 Sangiorgi et al., 2013; Saraga et al., 2011; Szigeti et al., 2014). Office buildings are generally
93 located in big cities near traffic intersections and busy roads in order to make them easily
94 accessible for the employees. These buildings are generally equipped with heating, ventilation
95 and air conditioning (HVAC) system to improve the air quality and create an acceptable feeling
96 of comfort for the office workers. The inlet of the HVAC system is generally located on the roof
97 of the buildings where the air is thought to be less polluted due to the distance from the traffic-
98 related sources compared to the ground level. The filtering effect of the mechanical ventilation
99 system, indoor sources and sinks of aerosol particles as well as the different microclimatic
100 conditions (i.e., temperature, relative humidity) all have an influence on the size and chemical
101 composition of the indoor particles as well as on the indoor/outdoor PM mass concentration ratio
102 (Meng et al., 2007). However, it is still a challenge to determine the indoor generated part of the
103 concentration of indoor PM_{2.5} mass and the PM constituents. Substantial fraction of outdoor
104 particulate matter pollution infiltrates indoors (Hänninen et al. 2004). Building occupants have
105 some influence on the infiltration by operating windows and doors and many studies have shown
106 that during the summer time infiltration levels are higher than in winter (Hänninen et al. 2011).

107 Many indoor activities (e.g., cooking, smoking, incense and candle burning) as well as re-
108 suspension of settled dust may contribute to indoor PM_{2.5} mass concentration in residential homes
109 (Urso et al., 2015); however, fewer indoor sources are apparent for offices. Particle emission
110 from printers, photocopiers and multi-task devices are well-known sources for ultra-fine particles,
111 but these have almost no impact on the PM_{2.5} mass concentration (e.g., Destailats et al., 2008; He
112 et al., 2007). Re-suspension of settled particles (with aerodynamic diameter larger than 1 μm)
113 from indoor surfaces are common particle sources in offices (Chatoutsidou et al., 2015). Some
114 specific activities (i.e., enveloping) could also contribute to the concentration of certain PM
115 constituents (Szigeti et al., 2014). Furthermore, *in-situ* ozone-initiated chemistry with reactive
116 volatile organic compounds could lead to the formation of secondary organic aerosol (Weschler

117 and Shields, 1999). However, it is likely that particles of outdoor origin are still the most
118 important determinants of $PM_{2.5}$ in these environments compared to the indoor generated
119 particles.

120 The spatial and temporal variation of particulate OP is not as well characterized as the mass
121 concentration and chemical composition of PM. Moreover, only a very limited information is
122 available about the OP of indoor PM. In the frame of the European Union project OFFICAIR (on
123 the reduction of health effects from combined exposure to indoor air pollutants in modern
124 offices), indoor and outdoor $PM_{2.5}$ samples were collected in office buildings to facilitate (i) the
125 OP assessment and chemical characterization of the particles and (ii) the investigation of the
126 relationship between particulate OP and PM constituents. Furthermore, the aim of this study was
127 to fill some gaps and answer some questions regarding the indoor and outdoor environment.

128

129 **2. Experimental**

130

131 **2.1. Description of sampling sites and instrumentation**

132

133 The selection of the office buildings was made according to predefined criteria developed during
134 the OFFICAIR project (Bluyssen et al., 2015). For highlighting regional similarities and
135 differences in aerosol characteristics, sampling sites were selected in different regions across
136 Europe. $PM_{2.5}$ samples were collected in Finland (FI), Greece (GR), Hungary (HU), Italy (IT)
137 and The Netherlands (NL) in a total of 20 office buildings ($n = 5$ for GR and HU, $n = 4$ for IT and
138 $n = 3$ for FI and NL). The location of the sampling sites is depicted in Fig. A.1. $PM_{2.5}$ was
139 sampled at one indoor and one outdoor location per building for approximately 100 h (from
140 Monday 9 AM until Friday 5 PM) during summer 2012. The sampling campaign was repeated in
141 winter 2012/2013. In order to investigate spatial variability within an office building, parallel
142 indoor sampling ($n = 2$) was performed in one Dutch building (NL3) in April and May 2013. The
143 indoor and concomitant outdoor $PM_{2.5}$ samples were collected onto quartz fiber filters (\varnothing 47 mm
144 and \varnothing 37 mm, Whatman QM-A) supplied by GE Healthcare (Little Chalfont, Buckinghamshire,
145 UK). Field blank samples were also collected. Before sampling, filters were wrapped in
146 aluminium foil and pre-treated at $550^{\circ}C$ in an electric oven for 8 h in order to eliminate any
147 possible organic contaminants. Thereafter filters were conditioned in an acclimatized room for 48

148 h at $20 \pm 1^\circ\text{C}$ and $50 \pm 5\%$ relative humidity, and then weighed on a Mettler Toledo XP26DR
149 balance with a readability of $2 \mu\text{g}$. Low-volume aerosol samplers equipped with a $\text{PM}_{2.5}$ head
150 operating at a constant flow rate of $0.24 - 2.3 \text{ m}^3 \text{ h}^{-1}$ were used. The sampling head was placed at
151 1.2 m height (sitting height) in the indoor locations. Two sampling strategies were applied for the
152 outdoor $\text{PM}_{2.5}$; at the air inlet of HVAC systems or at the same height as that which the indoor
153 sampling took place since, in some cases, it was not possible to perform the outdoor sampling at
154 the inlet of the HVAC system. In the case of Greece and Hungary, all buildings were selected in
155 the corresponding capital cities: Athens and its metropolitan area and Budapest. Two of the
156 Dutch monitored buildings were located in Delft, while one was in the resort settlement of
157 Noordwijk. Two of the Italian buildings chosen were in Florence, one in the center of Milan and
158 another one in the metropolitan area of Milan. Furthermore, office buildings located in a small
159 (Varkaus) and in a medium sized city (Kuopio) were selected in Finland. The main characteristics
160 of the monitored buildings are compiled in Table 1. The windows of the offices were generally
161 kept closed throughout the study; however, episodes of opened windows were registered during
162 the summer sampling campaign in some office buildings. During the sampling period, indoor and
163 outdoor air temperature and relative humidity were monitored close to the PM samplers with a
164 time resolution of 5 min.

165 *place of Table 1*

166

167 **2.2. Chemical characterization of $\text{PM}_{2.5}$**

168

169 Loaded as well as field blank filters were subjected to different chemical analyses in order to
170 determine the concentration of trace elements, major water-soluble ions as well as organic and
171 elemental carbon (OC and EC respectively) by the methods described in details elsewhere
172 (Mihucz et al., 2015). Briefly, 1/3 of each filter was cut out with a ceramic lance and then
173 subjected to vapor-phase microwave-assisted *aqua regia* extraction and the concentration of 16
174 trace elements (Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Mo, Cd, Sn, Sb and Pb) was
175 determined by inductively coupled sector field mass spectrometry (ICP-SF-MS; ELEMENT2;
176 ThermoFinnigan, Germany). Another 1/3 of each filter underwent a sonication-assisted water
177 extraction and the concentration of the major water-soluble ions and the water-soluble part of the
178 trace elements were determined by ion chromatography (881 Compact IC pro system; Metrohm,

179 Switzerland) and ICP-SF-MS respectively. One cm² of each filter was punched out and used for
180 the OC/EC analysis by means of an OC/EC analyzer (Sunset Laboratory, USA) and the default
181 temperature program of the EUSAAR-2 protocol (Cavalli et al., 2010). The sampling artefact of
182 OC was not investigated for the indoor and outdoor samples in this study. It should be noted that
183 the comprehensive chemical characterization of the PM_{2.5} samples collected in Finland and
184 Hungary was failed due to the low amount of PM collected as a result of the low air flow rate
185 (0.24 m³ h⁻¹) used during sampling.

186

187 **2.3 Assessment of particulate oxidative potential**

188

189 An acellular method based on the determination of antioxidant consumption was applied for the
190 assessment of the particulate OP. The extent to which these antioxidants are depleted by PM
191 reflects a direct measure of their oxidative activity. For this purpose, a synthetic RTLf containing
192 the antioxidants, urate, ascorbate and reduced glutathione in a physiologically relevant
193 concentration of 200 μmol L⁻³ each was prepared and used (Godri et al., 2010b; Szigeti et al.,
194 2014). Briefly, 5-mm discs (n=3) were punched from the loaded and field blank filters and
195 incubated at 37 °C for 4 h in 0.5 mL of the model RTLf. After centrifugation, the concentration
196 of urate and ascorbate was determined by reversed-phase high performance liquid
197 chromatography with electrochemical detection (Gilson Scientific Ltd., UK) based on a modified
198 method of Iriyima et al. (1984). Total glutathione and reduced glutathione were determined by
199 enzyme-linked 5,5'-dithio-bis(2-nitrobenzoic acid) assay by using a microplate reader
200 (SpectraMAX 190; Molecular Devices, UK) and based on the method of Baker et al. (1990). For
201 quality assurance, particle-free and known particle controls were run in parallel with the PM_{2.5}
202 samples. The detailed calculation method of the OP metrics has been described elsewhere (Godri
203 et al., 2010).

204

205 **2.4. Statistical data evaluation**

206

207 Pearson's linear (r) and Spearman's rank correlation coefficients (r_s) with a two-tailed test of
208 significance (p) were produced to show relationships between different PM characteristics by
209 using the software package of IBM SPSS Statistics for Windows, version 21 (IBM Corp.,

210 Armonk, NY, USA). Significant correlation was defined as $p < 0.05$. The Shapiro-Wilk test was
211 used to determine the distribution of data and subsequently the type of the correlation analysis
212 (parametric /Pearson's correlation/ or non-parametric /Spearman's rank correlation/).

213

214 **3. Results**

215

216 **3.1. Temporal and spatial patterns**

217

218 **3.1.1. PM_{2.5} mass concentration**

219

220 Table 2 presents the seasonal variability of the indoor and outdoor PM_{2.5} mass concentration as
221 well as the indoor/outdoor PM_{2.5} mass concentration ratio for each country. Considerable spatial
222 and temporal differences in the outdoor PM_{2.5} mass concentration values could be observed
223 among the study areas and seasons. The lowest average values were obtained in Finland for both
224 seasons, while the highest mean values were measured in Greece and in Hungary during summer
225 and winter respectively. The highest seasonal variation for outdoor PM_{2.5} mass concentration was
226 observed in Hungary where also the highest contrast was recorded between the ambient
227 temperature values during the summer (mean value: 26.3 °C) and the winter campaigns (mean
228 value: 3.6 °C).

229

place of Table 2

230 A strong correlation ($r=0.74$; $p<0.01$) was observed between the indoor and outdoor mass
231 concentration values. The indoor PM_{2.5} mass concentration was always lower than the
232 corresponding outdoor value, except for two cases when the outdoor PM_{2.5} mass concentration
233 was lower than 10 $\mu\text{g m}^{-3}$ in Finland and Italy. The indoor/outdoor PM_{2.5} mass concentration ratio
234 values obtained for the summer and the winter campaigns were compared (paired t-test) and no
235 association was found between them. Less than 20% difference in the indoor PM_{2.5} mass
236 concentration values was obtained in the case of the Dutch building where parallel indoor
237 sampling was carried out (Table A.1).

238

239 **3.1.2. Oxidative potential**

240

241 The OP of PM_{2.5} also varied markedly across the investigated sites (Fig. 1). Similar to our
242 previous observations, urate was not depleted by PM_{2.5} (e.g., Szigeti et al., 2014). To aid
243 interpretation, the OP metrics are depicted in OP^{AA} m⁻³ and OP^{GSH} m⁻³ (% depletion/m³ air) as
244 well as OP^{AA} μg⁻¹ and OP^{GSH} μg⁻¹ (% depletion/μg PM) units in Fig. 1. The former are considered
245 as exposure metrics, while latter ones point out the ability of the particles to deplete physically
246 relevant antioxidants.

247 *place of Fig. 1*

248 The maximum values for outdoor OP^{AA} m⁻³ and OP^{GSH} m⁻³ were about 30 and 90 times higher
249 than the lowest ones respectively. The lowest indoor and outdoor OP^{AA} m⁻³ and OP^{GSH} m⁻³ values
250 were obtained for PM_{2.5} collected in Finland, while the outdoor samples collected in Hungary
251 exhibited the highest activities during both seasons. In the case of indoor OP^{AA} m⁻³ and OP^{GSH} m⁻³
252 ³, PM_{2.5} samples collected in Hungary during winter showed the highest values. Seasonal
253 variation could be observed for both indoor and outdoor OP^{AA} m⁻³ and OP^{GSH} m⁻³ with higher
254 mean values during winter with some exceptions. On average, the mean indoor/outdoor OP^{AA} m⁻³
255 ratio was 0.64 (median: 0.60) and 0.78 (median: 0.71) for the summer and winter campaigns
256 respectively. A considerably larger seasonal difference was observed for the mean indoor/outdoor
257 OP^{GSH} m⁻³ ratio with values of 3.21 (median: 0.67) and 1.45 (median: 1.14) for summer and
258 winter respectively. The large difference in the mean and median OP^{GSH} m⁻³ values is due to the
259 outliers obtained in The Netherlands (e.g., maximum indoor/outdoor OP^{GSH} m⁻³ ratio of 25). The
260 indoor/outdoor OP^{AA} m⁻³ and OP^{GSH} m⁻³ ratio was larger than one in 4 and 17 cases out of the 40
261 respectively. Strong correlation was observed between the indoor and outdoor OP^{AA} m⁻³ (r_s=0.68;
262 p<0.01); however, indoor and outdoor OP^{GSH} m⁻³ values were not correlated (r_s=0.13).

263 The spatial and temporal variability was moderate for OP^{AA} μg⁻¹; however, substantial
264 differences were obtained for OP^{GSH} μg⁻¹ (Fig. 1). The highest outdoor OP^{AA} μg⁻¹ and OP^{GSH} μg⁻¹
265 values were apparent for Hungary and Italy during summer, while the PM_{2.5} samples collected in
266 The Netherlands showed the highest depletion rate for glutathione regarding the indoor
267 environment. The indoor/outdoor OP^{AA} μg⁻¹ and OP^{GSH} μg⁻¹ ratio was larger than one in 26 and
268 23 cases out of the 40 respectively. Indoor OP^{GSH} μg⁻¹ values were significantly higher than the
269 corresponding outdoor ones in the case of all samples collected in The Netherlands; however,
270 considerably lower outdoor OP^{GSH} μg⁻¹ levels were measured for the Dutch buildings compared
271 to the other office buildings.

272

273 3.1.3. Concentration of PM constituents and chemical mass closure

274

275 The contribution of the investigated PM constituents to the PM_{2.5} mass is depicted for the summer
276 and winter campaigns in Fig. 2. For the purpose of chemical mass closure, the concentration of
277 organic matter (OM = 1.6 × OC), sea salt (from standard seawater composition using Na⁺ as
278 tracer), non-sea-salt SO₄²⁻ ([nss-SO₄²⁻] = [SO₄²⁻] - 0.231 × [Na⁺]; the factor of 0.231 is the
279 average mass concentration ratio of SO₄²⁻ to Na⁺ in sea-water) and other ions (non-sea-salt
280 fraction of [Ca²⁺] + [Mg²⁺] + [K⁺]) were calculated. It should be noted that the approaches used
281 for the calculation of OM and sea salt contain uncertainty since (i) the average organic molecular
282 weight per carbon weight varies with location and season as the mix of organic compounds in
283 PM_{2.5} varies and (ii) it is assumed that the Na⁺ is only formed from sea spray.

284

place of Fig. 2

285 On average, 82% of the gravimetric mass could be reconstructed by the chemical measurements.
286 OM was the major component of the outdoor PM_{2.5} collected in Greece and in Italy for both
287 seasons, while NO₃⁻ represented the highest contribution in the case of PM_{2.5} collected in The
288 Netherlands. The relative contribution of OM to the mass of the indoor PM_{2.5} was higher than in
289 the case of the corresponding outdoor PM_{2.5} by factor of 1.5, on average. However, the
290 concentration of OM (expressed in μg m⁻³) was still lower in the indoor PM_{2.5} compared to the
291 outdoor PM_{2.5} in 82% of the cases due to the low indoor/outdoor mass concentration ratios.
292 Besides spatial variation, seasonality could also be observed for OM concentration with higher
293 values during winter for both indoor and outdoor PM_{2.5} while the concentration of EC was
294 relatively constant at all sites during summer and winter. However, higher EC concentration
295 values were observed for the office buildings located in big cities (Athens, Milan) with
296 significant road traffic than for those located in smaller cities (e.g., Noordwijk).

297 Among the major water-soluble ions, nss-SO₄²⁻, NO₃⁻ and NH₄⁺ were the dominant ions in both
298 indoor and outdoor PM_{2.5}. A winter peak was observed for the concentration of NO₃⁻; however,
299 no seasonality was observed for the concentration of nss-SO₄²⁻ in neither Italy nor The
300 Netherlands in contrast to Greece where the mean summer/winter concentration ratio was 2.2 and
301 2.3 for the indoor and outdoor PM_{2.5} respectively. The indoor/outdoor NO₃⁻ concentration ratio
302 was considerably lower than the corresponding indoor/outdoor PM_{2.5} mass concentration ratio

303 when the outdoor mean temperature value was lower than the indoor one suggesting the
304 evaporation of NH_4NO_3 (the main form of NO_3^- in $\text{PM}_{2.5}$) in the indoor environment. $\text{PM}_{2.5}$
305 samples collected in Milan were characterized by lower sea salt content since the sampling sites
306 were far from any coastal areas (>100 km) in contrast to Athens (<18 km) or Noordwijk (<1 km)
307 where the sea salt accounted for up to 8 and 26% of the $\text{PM}_{2.5}$ mass respectively. The sum of the
308 molar concentrations of the water-soluble cations multiplied with their corresponding charge was
309 almost equal to the sum calculated for the water-soluble anions (Fig. A.2). The median value of
310 the cations/anions ratios was 1.04 (0.80 – 1.39) and 1.07 (0.86 – 1.36) for the indoor and outdoor
311 $\text{PM}_{2.5}$ respectively.

312 The concentration of trace elements in the $\text{PM}_{2.5}$ varied widely among the sampling locations.
313 The minimum and maximum concentration values obtained for the offices were listed in a
314 previous publication (Mihucz et al., 2015). The indoor/outdoor trace element concentration ratios
315 expressed in $\text{ng m}^{-3}/\text{ng m}^{-3}$ and $\mu\text{g g}^{-1}/\mu\text{g g}^{-1}$ are depicted in Fig. A.3. The median values of the
316 indoor/outdoor trace element concentration ratios (expressed in $\text{ng m}^{-3}/\text{ng m}^{-3}$) were lower than
317 one; however, values higher than one were observed for Cr, Cu and Cd in more than 25% of the
318 cases. Regarding the indoor/outdoor ratios expressed in $\mu\text{g g}^{-1}/\mu\text{g g}^{-1}$, values higher than one were
319 observed for Cr, Cd, V, Rb, Sr, Pb, and Sn in more than 50% of the cases. The water-soluble
320 proportion of the elements expressed as the ratio of the concentration value obtained after water
321 extraction and the concentration value obtained after *aqua regia* extraction is shown in Fig. A.4.
322 The mean water soluble proportion was less than 25% for Al, Fe, Sn and Pb while the most
323 water-soluble elements were V and Zn. Considerable differences in the water-soluble proportions
324 could not be observed between the corresponding indoor and outdoor values. Similar water-
325 soluble proportion values were observed for the $\text{PM}_{2.5}$ collected in Greece and The Netherlands;
326 however, slightly different values were apparent in the case of some trace elements such as Sn,
327 Cr, Mn and Cd in Italy.

328

329 **3.2. Correlation between oxidative potential and PM characteristics**

330

331 Taking into account all $\text{PM}_{2.5}$ samples, significant correlation was observed between $\text{PM}_{2.5}$ mass
332 concentration and $\text{OP}^{\text{AA}} \text{ m}^{-3}$ ($r_s=0.71$, $p<0.01$). $\text{PM}_{2.5}$ mass concentration also correlated with
333 $\text{OP}^{\text{GSH}} \text{ m}^{-3}$ ($r_s=0.35$, $p<0.01$); however, the correlation was not as strong as in the case of $\text{OP}^{\text{AA}} \text{ m}^{-3}$

334 ³. In the case of $OP^{AA} \text{ m}^{-3}$, the correlation coefficient changed considerably when the samples
335 were grouped into indoor ($r_s=0.82$, $p<0.01$) and outdoor ($r_s=0.43$, $p<0.05$) subcategories. Smaller
336 deviation was observed between the correlation coefficients for the indoor ($r_s=0.21$, $p=0.23$) and
337 outdoor ($r_s=0.41$, $p<0.05$) $OP^{GSH} \text{ m}^{-3}$ and $PM_{2.5}$ mass concentration.

338 *place of Table 3*

339 Carbonaceous fractions and major water-soluble ions correlated poorly with the OP metrics
340 (Table 3) with some exceptions (e.g., OC and OP^{GSH}). Among the investigated trace elements,
341 only the concentration of Cu correlated with both $OP^{AA} \mu\text{g}^{-1}$ and $OP^{GSH} \mu\text{g}^{-1}$ in the case of both
342 indoor and outdoor $PM_{2.5}$. We noted considerable differences between the correlation coefficients
343 obtained for the indoor and outdoor $PM_{2.5}$. Significant positive correlations between the
344 concentration of 8 trace elements (Cu, Ni, Sn, Cd, Fe, Cr, Co and Pb) and $OP^{AA} \mu\text{g}^{-1}$ were
345 apparent for the outdoor $PM_{2.5}$. In contrast, only 2 trace elements (Cu and Mo) were relevant in
346 the case of indoor $PM_{2.5}$. A similar trend could be observed for the correlation coefficients
347 obtained between the water-soluble part of the trace element and $OP^{AA} \mu\text{g}^{-1}$. Fewer trace elements
348 showed significant correlation with $OP^{GSH} \mu\text{g}^{-1}$ compared to $OP^{AA} \mu\text{g}^{-1}$ for both the indoor and
349 outdoor $PM_{2.5}$.

350

351 **4. Discussion**

352

353 **4.1. Geographical location, outdoor PM sources, infiltration and indoor PM sources: Which**
354 **are the major determinants of indoor $PM_{2.5}$ mass concentration?**

355

356 The outdoor $PM_{2.5}$ mass concentration values obtained in our study are consistent with the results
357 reported elsewhere for the same areas (e.g., Kassomenos et al., 2014; Marcazzan et al., 2011;
358 Putaud et al., 2010; Sillanpää et al., 2006; Szigeti et al., 2015). It is well-known that urban $PM_{2.5}$
359 mass concentration values are generally higher in Central and Southern Europe than in Northern
360 Europe and most of the cities have difficulties with keeping the $PM_{2.5}$ mass concentration below
361 the annual $PM_{2.5}$ mass concentration limit value ($25 \mu\text{g m}^{-3}$; EC, 2008). In line with this
362 statement, considerably lower $PM_{2.5}$ mass concentration values were apparent for the sites
363 investigated in Finland and in The Netherlands compared to Greece, Hungary and Italy.

364 Generally, only the indoor/outdoor concentration ratio is used to get information regarding
365 whether people are exposed to higher concentration indoors or outdoors. However, this simple
366 parameter does not allow for separating the outdoor particles from those generated indoors.
367 Another approach estimates the infiltration factor as well as the amount of the indoor generated
368 particles by using a marker compound which has no indoor source such as SO_4^{2-} (e.g., Hanninen
369 et al., 2004; Sangiorgi et al., 2013). Moreover, the enrichment of an element in the indoor PM can
370 be evaluated by calculating the indoor enrichment factor (EF) which is the ratio of the crustal EF
371 of a constituent for the indoor PM to the crustal EF of the same constituent for the corresponding
372 outdoor PM (Salma et al., 2013; Sziget et al., 2014). One of the drawbacks of these methods is
373 that there is no parameter which would take into account the evaporation of the semi-volatile
374 compounds (e.g., NH_4NO_3) due to the change of temperature when outdoor particles penetrate
375 into the offices.

376 Since (i) a strong correlation was observed between the indoor and outdoor $\text{PM}_{2.5}$ mass
377 concentration values; (ii) the indoor/outdoor $\text{PM}_{2.5}$ mass concentration ratio was generally lower
378 than one and (iii) the indoor/outdoor concentration ratio was also lower than one for all PM
379 constituents with some exceptions, it can be assumed that, in general, the indoor $\text{PM}_{2.5}$ was not
380 affected by any substantial indoor sources and the outdoor $\text{PM}_{2.5}$ mass concentration was still the
381 major factor. It is also clear that the physical position and the proper operation of the HVAC
382 system (e.g., efficient filtration; optimal air exchange rate) is important to reduce the PM mass
383 concentration (Morawska et al., 2009; Quang et al., 2013); however, the determination of the
384 exact infiltration rate is still challenging; the selection of the indoor and outdoor sampling
385 locations, the frequency of windows opening; the filtering efficiency of the bag filters for the
386 different particle sizes as well as the size distribution of the PM constituents all having an
387 influence besides the evaporation of the semi-volatile compounds, sink (e.g., deposition on
388 indoor surfaces), re-suspension and generation of aerosol particles. For example, it has been
389 shown that an upgrade on the HVAC system could increase the overall efficiency of the system
390 in removing particles from 58 to 86% (Morawska et al., 2009). Furthermore, the higher
391 indoor/outdoor concentration values observed for some trace elements (e.g., Cd, Cu, Cr) in some
392 cases suggest that they might have indoor sources. For example, Cd and Cr are associated with
393 tobacco smoke (Slezakova et al., 2009) and office workers might take these compounds adsorbed
394 on their clothes, skin or hair into the offices (thirdhand smoke).

395

396 **4.2. Indoor air vs. outdoor air: Where is it better to stay?**

397

398 If we approach the question from the angle of the $PM_{2.5}$ mass concentration, it is better to stay
399 indoors than outdoors irrespective of the season since the indoor/outdoor $PM_{2.5}$ mass
400 concentration ratios were less than one for the office buildings with only two exceptions.
401 However, recent epidemiological studies focus on the chemical composition of PM, on the
402 identification of those PM constituents which may be responsible for health outcomes and on the
403 toxicologically relevant features of PM rather than the $PM_{2.5}$ mass concentration. The comparison
404 of the mean indoor/outdoor $OP^{AA} m^{-3}$ and $OP^{GSH} m^{-3}$ ratios with the mean indoor/outdoor $PM_{2.5}$
405 mass concentration ratio revealed that the mean indoor/outdoor ratios for the OP metrics were
406 larger than the mean indoor/outdoor $PM_{2.5}$ mass concentration ratio especially in the case of
407 $OP^{GSH} m^{-3}$. Furthermore, the indoor/outdoor ratios for $OP^{AA} m^{-3}$ and $OP^{GSH} m^{-3}$ were larger than
408 one in more cases than the indoor/outdoor $PM_{2.5}$ mass concentration ratio; however, the mean
409 indoor/outdoor ratio for the $OP^{AA} m^{-3}$ was still lower than one, and similarly, the mean
410 indoor/outdoor ratio for $OP^{GSH} m^{-3}$ was lower than one in more than 50% of the cases. These OP
411 results also suggest that staying indoors is generally better than spending time outdoors.
412 However, the indoor/outdoor $OP^{AA} m^{-3}$ and $OP^{GSH} m^{-3}$ ratios only imply whether office workers
413 are exposed to oxidatively more challenging air indoors than outdoors or not. The considerable
414 spatial and temporal differences observed for the OP metrics suggest that the office building
415 characterized by indoor/outdoor $OP^{AA} m^{-3}$ and $OP^{GSH} m^{-3}$ ratios lower than one might have more
416 health relevance compared to those characterized by ratios higher than one when the absolute
417 indoor OP values are compared.

418 If the title of this section was “Indoor particles vs. outdoor particles: Which particles are
419 considered to be more relevant in terms of OP?” then the answer would be less favorable for the
420 indoor environment since the indoor particles generally showed considerably larger oxidative
421 activity (especially $OP^{GSH} \mu g^{-1}$) than the outdoor particles on a per unit mass basis in our study.
422 This observation (i.e., indoor/outdoor $OP^{GSH} \mu g^{-1}$ and $OP^{AA} \mu g^{-1}$ ratios were generally higher than
423 the corresponding indoor/outdoor $OP^{GSH} m^{-3}$ and $OP^{AA} m^{-3}$ ratios) might be caused by several
424 issues such as (i) the evaporation of those PM constituents which are not relevant in terms of OP
425 in the indoor environment or (ii) higher filtration efficiency for the above-mentioned compounds

426 or (iii) the formation of reactive oxygen species in the indoor environment. This approach for the
427 assessment of the OP is not relevant in terms of occupational exposure; however, it compares the
428 ability of the indoor and outdoor particles to deplete physically relevant antioxidants.

429 The intensive investigation of PM oxidative activity through antioxidant depletion assays dates
430 back to the early 2000s; several studies have been carried out at outdoor sites with different
431 source characteristics (e.g., Font et al., 2014; Godri et al., 2010, 2011; Janssen et al., 2014);
432 however, little is known about the OP of indoor PM. In our previous study we investigated the
433 OP of PM_{2.5} collected in Hungarian office buildings during the 8-h day shift (Szigeti et al., 2014).
434 Similar to this study, higher OP^{GSH} μg⁻¹ results were obtained for the indoor PM_{2.5} compared to
435 the corresponding outdoor data in three office building out of the five. To the best of our
436 knowledge, there is no other published study about OP of indoor PM. A more complex
437 investigation of the air pollutants is needed to fully answer the original question since there are
438 also other health relevant air pollutants (e.g., formaldehyde, NO₂, O₃) and other health effects
439 associated to PM constituents.

440

441 **4.3. Linkage between PM constituents and particulate oxidative activity: Which are the** 442 **relevant PM constituents?**

443

444 Our findings on the correlations between the OP of outdoor PM and the concentration of PM
445 constituents are in good agreement with previous observations (e.g., Godri et al., 2010, 2011;
446 Künzli et al., 2006; Nawrot et al., 2009; Szigeti et al., 2015; Yang et al., 2014). Previous studies
447 have shown that OP^{AA} and OP^{GSH} are sensitive to slightly different panels of metals and PM
448 sources; OP^{GSH} is sensitive to traffic-related trace elements and OP^{AA} is more sensitive to
449 regional PM constituents (e.g., Kelly et al., 2011). The statistical analysis revealed some
450 differences for OP^{AA} and OP^{GSH}; more aerosol constituents were linked to OP^{AA} than OP^{GSH} as
451 well as considerable differences were observed in the case of indoor and outdoor PM_{2.5}.
452 However, the source apportionment analysis failed due to the low number of samples collected at
453 each site. Previous studies have found heterogeneous associations between particulate oxidative
454 activity and the concentration of PM constituents across European sites (Künzli et al., 2006;
455 Nawrot et al., 2009) which may explain the low correlation coefficients observed for some PM
456 constituents since all results for PM_{2.5} collected in Greece, Italy and The Netherlands were

457 included in the correlation analysis. The heterogeneity may derive from the differences in the
458 oxidation state, the chemical form as well as the bioavailable part of the same trace element at
459 different sites since the sampling locations were characterized by different PM sources and
460 meteorological conditions. The differences observed among the sites for the water-soluble
461 proportions of the trace elements (Fig. A.4) also strengthen this assumption. In the case of the
462 indoor PM_{2.5}, the weaker correlations suggest that the link between particulate OP and PM
463 constituents is a more complex issue compared to the outdoor PM_{2.5} and that the indoor air
464 chemistry might play a crucial role in the formation of reactive oxygen species and other
465 compounds which alter the oxidative properties of PM.

466 The pathways of particle-induced toxicity through antioxidant loss at the air–lung interface have
467 already been discussed (Kelly and Fussell, 2012) and the trace elements (e.g., Cu, Sn, Ni, Fe)
468 which showed strong and moderate correlations with the OP metrics in our study are in line with
469 the proposed mechanism. The role of the water-soluble part of the trace elements does not appear
470 to be significant since similar correlation coefficients were obtained between them and the OP
471 metrics compared to the corresponding values obtained for the total trace element concentrations.
472 However, firm conclusions cannot be made since the heterogeneity observed across the sites may
473 have an effect as well. OC has not previously been identified as an indicator of OP^{GSH}; however,
474 earlier studies found associations between particulate OP and water-soluble organic carbon
475 (Szigeti et al., 2015; Verma et al., 2012). The link between the OP metrics and EC might be
476 caused by some redox active compounds (i.e., quinones) adsorbed at the surface of the EC rather
477 than by EC itself. There is no simple explanation for the associations observed between some
478 major soluble ions and OP metrics.

479

480 **4.4. Spatial variability in an office building: How to perform representative indoor PM** 481 **sampling?**

482

483 The lack of any major indoor PM sources and by applying similar air exchange rates, it is
484 expected that the PM_{2.5} mass concentration values are similar in all offices in a modern building
485 if the same mechanical ventilation system is used to supply fresh air into the offices. In the case
486 of the Dutch office building (NL3), we obtained quite similar PM_{2.5} mass concentration values
487 for the two different offices in which the monitoring campaigns were performed simultaneously.

488 However, a larger deviation was observed for the OP metrics as well as for the concentration of
489 the minor and trace PM constituents (Table A.1). The offices selected for this study were located
490 on the same floor, with similar room dimensions, exactly the same flooring, wall and ceiling
491 materials and office layouts. The rooms were not occupied by office workers during the sampling
492 campaign, the windows were kept closed and the difference in the air exchange rate values were
493 less than 5%. Consequently, it can be stated that the distribution of the minor and trace PM
494 constituents was not homogenous in the air of the office building. Both PM_{2.5} samplers were
495 applied a flow rate of 16.7 L min⁻¹ which is comparable with the inhaled air volume of a healthy
496 male and female doing sitting activity (approximately 9 and 6.5 L min⁻¹ for males and females
497 respectively; calculated from the tidal volume and breathing cycle) as recommended by ICRP66
498 (1994). These findings suggest that the office workers may be exposed to health relevant PM
499 constituents to a different extent within the same office building even if the parameters of indoor
500 environment are similar for the offices.

501

502 **4.5. Limitations of the study**

503

504 This study is the first large-scale investigation of PM_{2.5} oxidative activity in office buildings
505 across Europe; however, the low number of samples collected at each site does not allow us to
506 make any substantial comparison among the individual buildings.

507 It should be noted that the long sampling time (about 100 h) could lead to a bias in the
508 determination of the real PM_{2.5} exposure of office workers. For comparison, 8-h long PM_{2.5}
509 sampling was also carried out during the working hours in the Hungarian office buildings in a
510 selected office (different (HU1-3) or same (HU4-5) office than in this study) and at the air inlet of
511 the HVAC system (next to the sampling device used in this study) (Szigeti et al., 2014). The
512 deviation was less than 23% between the indoor PM_{2.5} mass concentration values obtained for the
513 8-h daily and the 100-h PM_{2.5} samples and less than 18% for the indoor/outdoor mass
514 concentration ratio with one exception (HU5). On average, the indoor PM_{2.5} mass concentration
515 was only 6% higher in the case of the 8-h PM_{2.5} samples which indicates that the long sampling
516 time might not lead to significant underestimation regarding indoor PM_{2.5} mass concentration.
517 Furthermore, less chemical analysis could be carried out in the case of samples collected by low-

518 volume aerosol samplers during the 8-h day shift since the collected PM mass was considerably
519 lower compared to this study.

520 We assessed particulate OP through antioxidant depletion; however, other acellular assays are
521 available with still no consensus regarding which one would characterize better the oxidative
522 activity of PM. The different assays are sensitive towards different PM components (Ayres et al.,
523 2003). However, the same methodology was used for the assessment of OP of PM collected at
524 different environments which makes the comparison across these studies easier (e.g., Szigeti et
525 al., 2014, 2015).

526 The strong correlation among PM constituents (especially in the case of trace elements) may
527 cause false associations when the link between OP metrics and PM constituents is investigated.
528 This limitation will not help to fully understand the mechanism; however, the identification of the
529 major PM sources responsible for antioxidant depletion might be possible by multivariate
530 statistics.

531 Since many trace elements may originate from different sources, it would be an advantage to
532 have information about the chemical form of the elements which would help in the source
533 apportionment as well as in the understanding of the mechanism behind the particle-induced
534 toxicity. However, current instrumental analytical techniques are not capable to perform
535 speciation analysis for many elements at trace levels.

536

537 **5. Conclusions**

538

539 As people spend most of their time in indoor environments, indoor air quality receives more and
540 more attention. In the case of office buildings equipped with HVAC system, it seems that outdoor
541 air pollution is the major factor affecting indoor PM_{2.5} mass concentration. Furthermore, several
542 parameters such as the overall efficiency of the mechanical ventilation system as well as the
543 frequency of the windows openings determine the actual indoor PM_{2.5} levels. Results suggest that
544 the indoor sources of PM_{2.5} mass concentration might be less important in office building if
545 special activity is not carried out in the offices. Accordingly, to set a target value for the indoor
546 PM_{2.5} mass concentration might not be a priority issue in office buildings in contrast to the
547 reduction of the outdoor PM_{2.5} mass concentration by different regulations (e.g., introduction of
548 low emission zones). However, office buildings with larger indoor/outdoor PM_{2.5} mass

549 concentration ratio values may require reconsideration of the performance of ventilation system.
550 Both $OP^{AA} \text{ m}^{-3}$ and $OP^{GSH} \text{ m}^{-3}$ were generally lower indoors than outdoors; however, several
551 offices exhibited indoor/outdoor values higher than one.

552 Some questions still remain unanswered. It is clear that traffic-related trace elements (e.g., Cu)
553 are the major determinants of particulate OP; however, results suggest that indoor air chemistry
554 may also play an important role in the OP of indoor $PM_{2.5}$. Further investigation is also needed on
555 the distribution of health relevant PM constituents in indoor air.

556

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558

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568

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Table 1. Characteristics of the office buildings.

Building ID	Completion year	Location	Outdoor source for air contamination (< 50 m)	Total number of storeys (storey number for indoor sampling)	Intake position of HVAC systems (m)	Outdoor sampling height (m)
FI1	2009	Kuopio; commercial/residential area	car parking, busy road	6 (2)	façade (25 m)	4
FI2	2003	Varkaus, industrial, residential area	car parking, railway	4 (2)	façade (10 m)	1.5
FI3	2004	Varkaus; city center, densely packed housing	car parking, busy road	3 (2)	façade (12 m)	1.5
GR1	2003	Athens; suburban, with larger gardens	car parking	2 (0)	façade (8 m)	1.5
GR2	2004	Athens; commercial area	busy road, quarry works	2 (1)	façade (25 m)	3.5
GR3	2010	Athens; commercial/residential area	busy road, railway station	7 (3)	roof (20 m)	13.5
GR4	1994	Athens; industrial area	car parking, busy road, highway	2 (0)	roof (10 m)	1.5
GR5	1996 ^a	Athens; industrial area	car parking	2 (2)	roof (8 m)	3.5
HU1	2007	Budapest; commercial/residential area	busy road	8 (4)	façade (30 m)	30
HU2	2006	Budapest; commercial/residential area	car parking, busy road	16 (11)	roof (65 m)	66
HU3	1995	Budapest; city center, densely packed housing	car parking, busy road	11 (3)	roof (37 m)	38
HU4	2008	Budapest; commercial/residential area	car parking, busy road, railway	8 (3)	roof (27 m)	28
HU5	2009	Budapest; industrial/residential area	car parking, busy road	8 (3)	roof (30 m)	31
IT1	1970	Milan; commercial area	car parking	7 (2)	roof (25 m)	10
IT2	2006	Milan; commercial area	car parking, low-traffic road	5 (3)	roof (20 m)	15
IT3	2009	Florence; commercial/residential area	car parking	4 (2)	roof (22 m)	22
IT4	2009	Florence; commercial/residential area	car parking	4 (2)	roof (22 m)	15
NL1	1965	Noordwijk; rural area	car parking	4 (3)	roof (15 m)	16
NL2	1999	Delf; industrial/residential area	car parking, busy road	5 (1)	roof (20 m)	21
NL3	2003	Delf; commercial/residential area	car parking	7 (3)	roof (30 m)	31

^a The building was converted in 2000.

Table 2. Minimum, mean and maximum mass concentration ($\mu\text{g m}^{-3}$) of indoor and outdoor $\text{PM}_{2.5}$ as well as the indoor/outdoor $\text{PM}_{2.5}$ mass concentration ratios observed for the summer and winter sampling campaigns. Median values are also indicated for the larger dataset.

	PM _{2.5} mass concentration ($\mu\text{g m}^{-3}$; min - mean (median) - max)				indoor/outdoor mass concentration ratio (min – mean (median) - max)	
	summer		winter		summer	winter
	indoor	outdoor	indoor	outdoor		
FI	2.6 - 3.4 - 5.3	3.7 - 7.5 - 12.0	3.4 - 4.8 - 6.3	4.8 - 6.2 - 8.7	0.35 - 0.50 - 0.71	0.66 - 0.80 - 1.02
GR	8.7 - 13.3 - 16.8	14.5 - 25.4 - 31.2	5.5 - 14.3 - 18.5	9.5 - 20.8 - 26.0	0.45 - 0.53 - 0.60	0.57 - 0.68 - 0.86
HU	5.5 - 9.4 - 17.1	9.3 - 16.2 - 27.8	12.9 - 21.3 - 32.3	34.7 - 41.1 - 47.3	0.28 - 0.62 - 0.94	0.27 - 0.52 - 0.73
IT	8.9 - 10.5 - 12.6	9.3 - 10.1 - 11.1	6.1 - 11.0 - 17.7	8.6 - 27.8 - 62.4	0.89 - 1.05 - 1.35	0.28 - 0.58 - 0.73
NL ^a	4.2 - 5.2 - 6.1	9.4 - 10.8 - 12.2	5.0 - 8.4 - 12.8	6.1 - 23.7 - 33.6	0.42 - 0.48 - 0.58	0.24 - 0.48 - 0.81
<i>All</i>	<i>2.6 - 9.0 (8.7) - 17.1</i>	<i>3.7 - 15.4 (12.1) - 31.2</i>	<i>3.4 - 13.2 (12.9) - 32.3</i>	<i>6.1 - 25.4 (25.5) - 62.4</i>	<i>0.28 - 0.62 (0.58) - 1.35</i>	<i>0.24 - 0.61 (0.58) - 1.02</i>

^a Additional samples collected in April and May 2013 are included in winter and summer results respectively.

Abbreviations: FI = Finland; GR = Greece; HU = Hungary; IT = Italy; NL = The Netherlands

Table 3. Spearman's rank correlation coefficients between particulate oxidative potential (OP^{AA} μg^{-1} and OP^{GSH} μg^{-1}) and the concentration ($\mu\text{g g}^{-1}$) of the investigated aerosol constituents. Significant correlations are highlighted.

	OP^{AA}			OP^{GSH}		
	indoor (n=24)	outdoor (n=22)	all sites (n=46)	indoor (n=24)	outdoor (n=22)	all sites (n=46)
<i>Carbonaceous fractions</i>						
OC	-0.06	0.37	0.30	0.07	0.71**	0.48**
EC	0.13	0.49*	0.30	0.05	0.52*	0.29
<i>Major water-soluble ions</i>						
NH_4^+	-0.15	-0.14	-0.12	-0.39	-0.46	-0.38
Na^+	0.14	-0.02	0.03	0.21	-0.22	-0.03
K^+	-0.24	0.63**	0.33*	-0.19	0.35	0.17
Ca^{2+}	-0.22	-0.20	-0.30	-0.14	-0.18	-0.25
Mg^{2+}	0.08	0.01	-0.01	0.31	0.00	0.11
SO_4^{2-}	-0.04	0.13	0.08	-0.16	-0.30	-0.12
NO_3^-	0.29	-0.20	-0.03	0.78**	-0.31	0.13
Cl^-	0.37	-0.40	-0.08	0.53**	-0.27	0.08
<i>Aqua regia extractable part of trace elements</i>						
Al	-0.15	0.30	0.07	0.04	0.42	0.15
V	0.07	0.42	0.23	0.17	-0.02	0.09
Cr	0.25	0.44*	0.44**	-0.02	0.23	0.13
Mn	0.01	0.28	0.05	-0.19	0.15	-0.11
Fe	-0.13	0.46*	0.11	-0.59	0.37	-0.18
Co	0.15	0.43*	0.19	0.22	0.08	0.08
Ni	0.18	0.59**	0.34*	0.19	0.29	0.26
Cu	0.48*	0.87**	0.67**	0.65**	0.48*	0.58**
Zn	0.13	0.40	0.24	-0.34	0.03	-0.16
Rb	-0.07	0.37	0.16	-0.37	0.07	-0.14
Sr	0.14	0.31	0.23	0.40	0.24	0.32*
Mo	0.44*	0.23	0.30*	0.50*	0.10	0.32*
Cd	0.16	0.49*	0.44**	-0.10	0.53*	0.33*
Sn	0.32	0.53*	0.42**	0.42*	0.76**	0.52**
Pb	0.14	0.43*	0.34*	0.05	0.22	0.19
<i>Water-soluble part of trace elements</i>						
Al	-0.28	0.51*	0.13	-0.29	0.47*	0.00
V	0.11	0.41	0.24	0.18	-0.03	0.09
Cr	0.25	0.44*	0.41**	-0.02	0.29	0.16

Mn	0.04	0.04	-0.10	-0.30	-0.15	-0.38
Fe	0.21	0.75**	0.39**	-0.42	0.34	-0.20
Co	0.13	0.17	0.04	0.38	-0.34	0.01
Ni	0.23	0.56**	0.35*	0.20	0.13	0.16
Cu	0.43*	0.76**	0.58*	0.59**	0.53*	0.54**
Zn	0.17	0.36	0.23	-0.37	-0.02	-0.20
Rb	0.05	0.29	0.19	-0.44	-0.01	-0.23
Sr	0.07	0.20	0.12	0.23	0.12	0.13
Mo	0.39	0.26	0.33*	0.35	0.15	0.27
Cd	0.01	0.53*	0.38**	-0.37	0.38	0.09
Sn	0.10	0.41	0.41**	0.03	0.19	0.22
Sb	0.39	0.61**	0.55**	0.03	0.38	0.23
Pb	0.14	0.35	0.32*	0.01	0.01	0.07

* p<0.05 level

** p<0.01 level

Figure Captions

Figure 1. Seasonal and spatial variation of ascorbate and glutathione oxidative potential per unit volume ($OP^{AA} \text{ m}^{-3}$ /a/ and $OP^{GSH} \text{ m}^{-3}$ /b/;% depletion/ m^3 air; mean \pm standard deviation) and per unit mass ($OP^{AA} \mu\text{g}^{-1}$ /c/ and $OP^{GSH} \mu\text{g}^{-1}$ /d/;% depletion/ μg PM; mean \pm standard deviation) for the indoor and outdoor $PM_{2.5}$.

Abbreviation: LOD = limit of detection

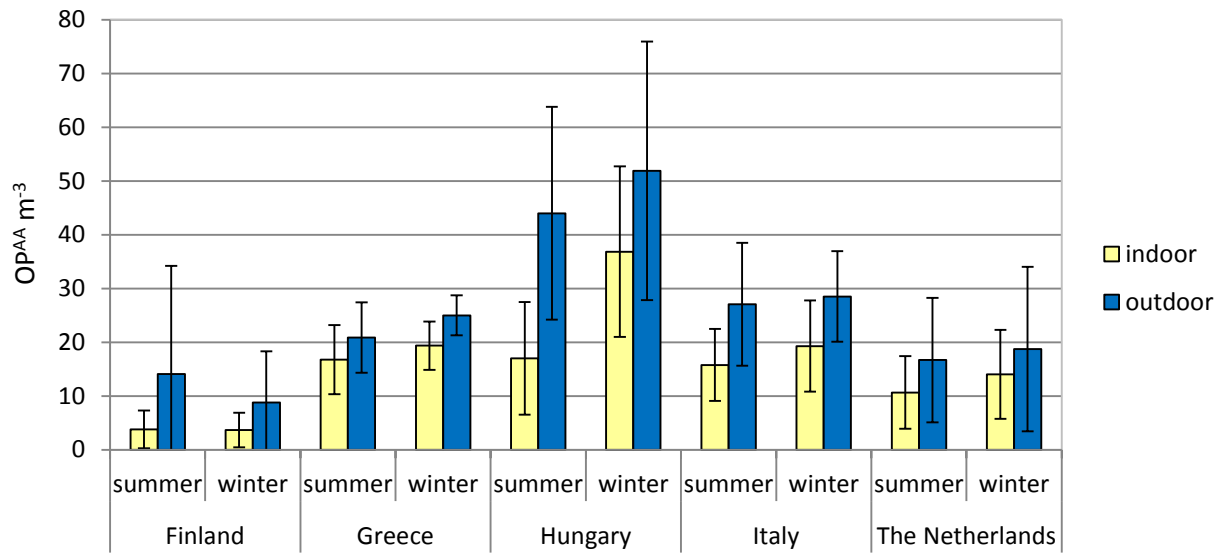
Figure 2. Contribution (expressed in %) of the PM constituents to the indoor and outdoor $PM_{2.5}$ mass during summer (a) and winter (b). The outdoor mean temperature values are also indicated.

*Samples were collected in spring (April and May); however, they are depicted among the other results obtained for the samples collected in summer (May) and winter (April).

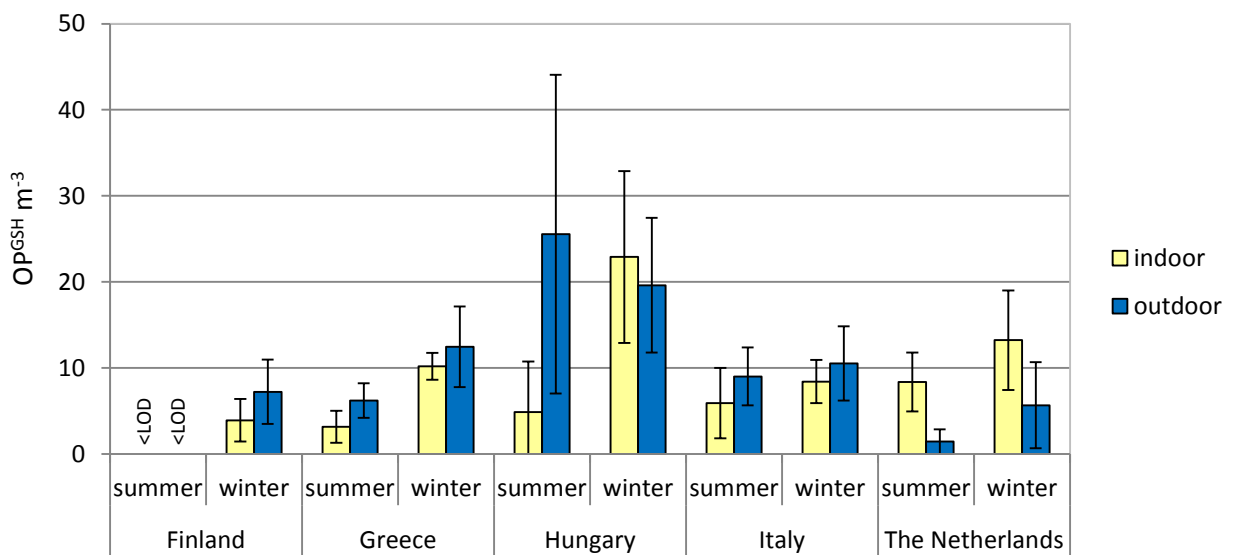
Abbreviations: OM = organic matter; EC = elemental carbon; nss-sulfate = non-sea-salt sulfate

Figure 1

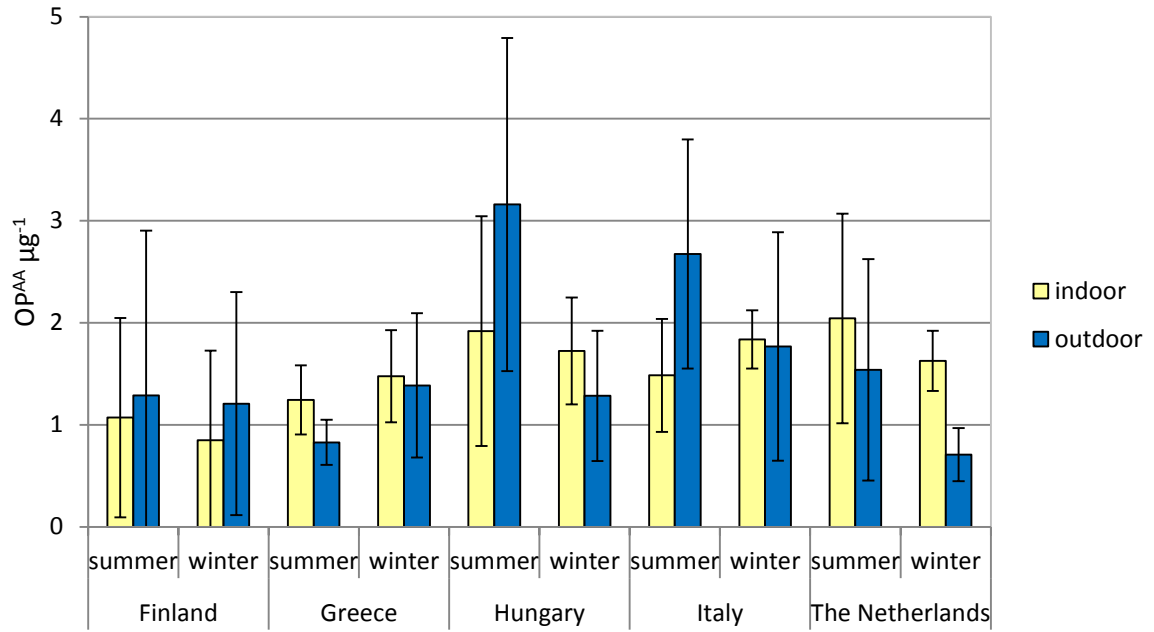
a



b



c



d

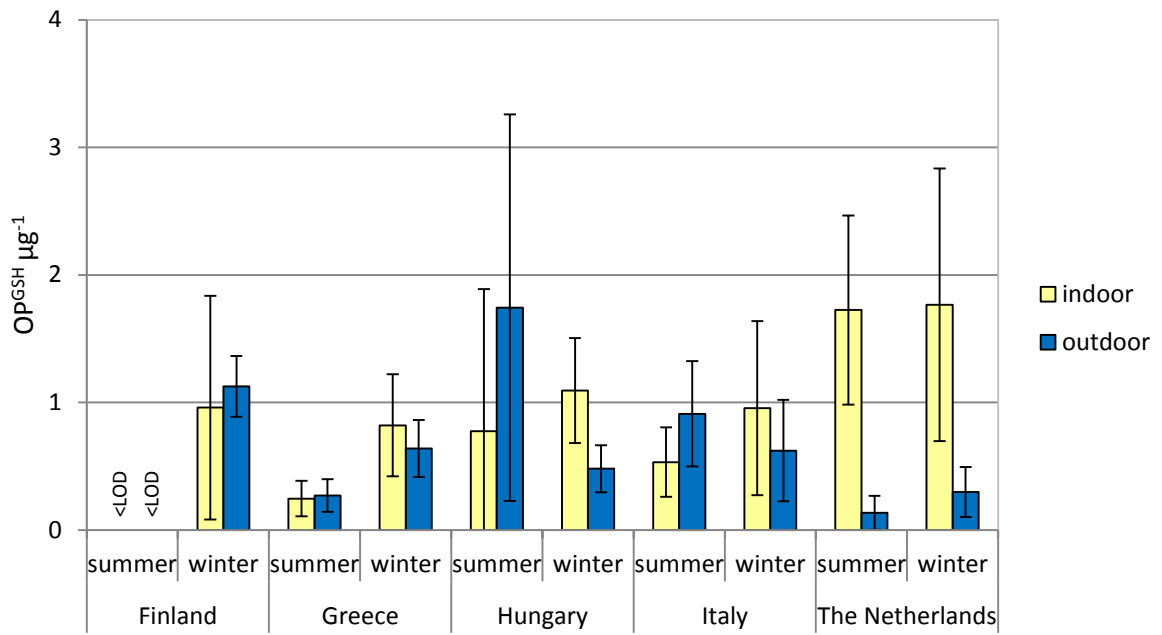
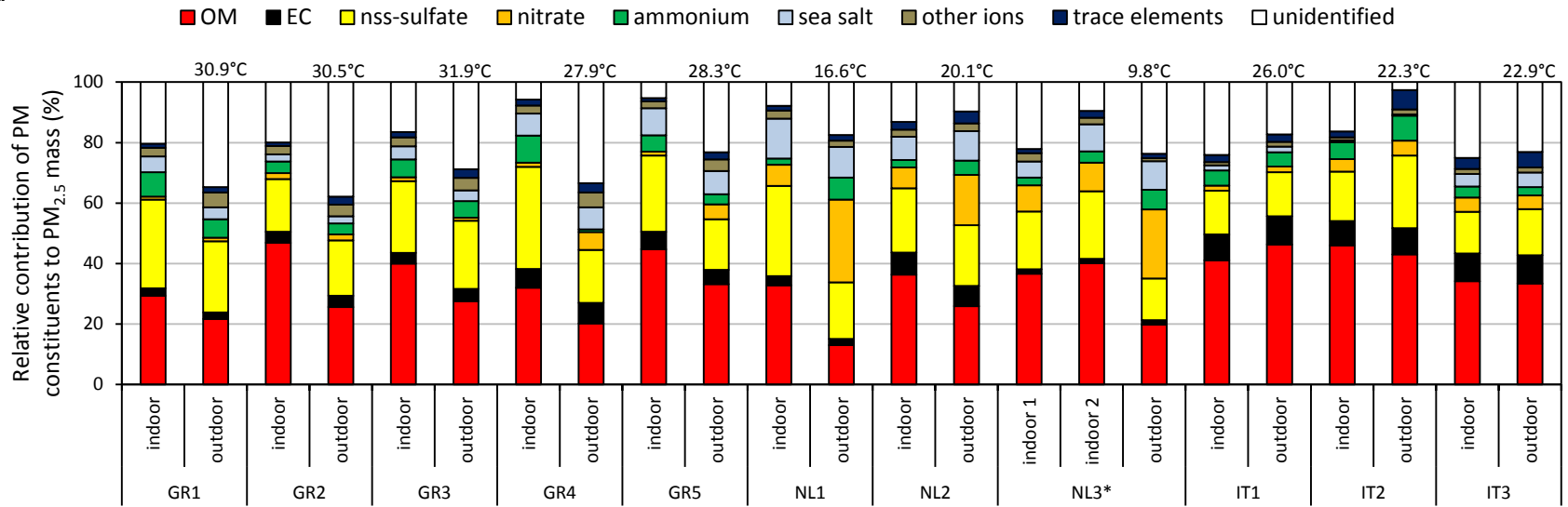
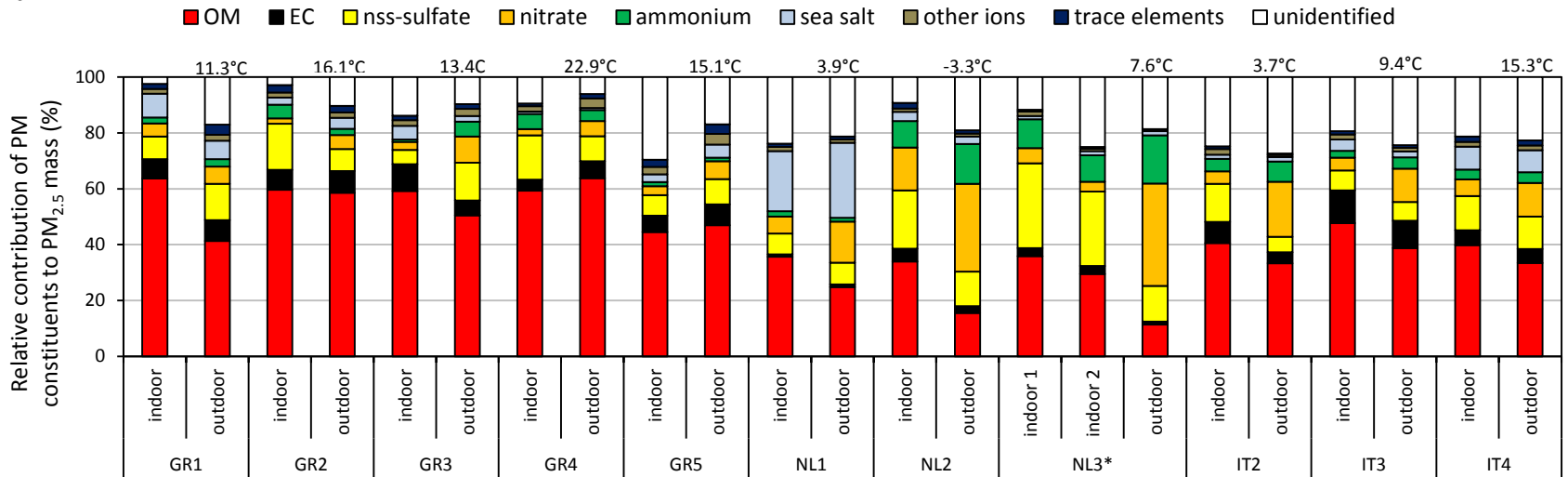


Figure 2

a



b



Highlights

- PM_{2.5} mass concentration and oxidative potential (OP) varied markedly across Europe.
- The I/O PM_{2.5} mass concentration ratio was less than one with two exceptions.
- Generally, it is better to stay indoors than outdoors regarding particulate OP.
- OP metrics were associated mainly with traffic-related trace elements (e.g., Cu).
- Indoor air chemistry may play an important role in the OP of indoor PM.

SUPPORTING INFORMATION

Oxidative potential and chemical composition of PM_{2.5} in office buildings across Europe – The OFFICAIR study

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Table A.1. Concentration of PM_{2.5} mass and the investigated constituents as well as the oxidative potential (OP^{AA} m⁻³, OP^{GSH} m⁻³) for the indoor and outdoor samples collected at NL3. The deviation between the results obtained for the two parallel indoor samples are also listed.

	winter campaign			summer campaign			deviation between indoor 1 and 2 (%; ^a)	
	indoor 1	indoor 2	outdoor	indoor 1	indoor 2	outdoor	winter campaign	summer campaign
<i>mass concentration (µg m⁻³)</i>								
PM _{2.5}	6.82	8.24	31.4	4.24	4.10	9.44	21	-3
<i>oxidative potential (per m³)</i>								
OP ^{AA}	9.43 ± 1.05	14.2 ± 1.5	19.5 ± 3.0	3.18 ± 1.41	6.90 ± 0.74	6.84 ± 0.99	51	117
OP ^{GSH}	5.78 ± 2.89	11.7 ± 1.2	2.67 ± 0.71	4.13 ± 1.37	9.81 ± 0.35	0.71 ± 0.92	102	138
OP ^{TOT}	15.2 ± 3.9	25.9 ± 2.7	22.2 ± 3.7	7.31 ± 2.78	16.7 ± 1.1	7.55 ± 1.91	70	128
<i>carbonaceous compounds (µg m⁻³)</i>								
OC	1.53	1.52	2.23	0.97	1.03	1.17	-1	6
EC	0.19	0.23	0.34	0.06	0.06	0.13	18	-5
<i>major water-soluble ions (µg m⁻³)</i>								
NH ₄ ⁺	0.71	0.78	5.43	0.11	0.15	0.61	11	42
Na ⁺	0.04	0.06	0.12	0.15	0.23	0.43	28	54
K ⁺	0.08	0.06	0.09	0.07	0.04	0.04	-21	-50
Ca ²⁺	0.03	0.01	0.05	0.06	0.07	0.09	-65	27
Mg ²⁺	0.01	0.01	0.03	0.03	0.03	0.05	-19	7
SO ₄ ²⁻	2.09	2.21	4.03	0.84	0.98	1.41	6	16
NO ₃ ⁻	0.36	0.29	11.5	0.37	0.39	2.16	-20	4
Cl ⁻	0.02	0.04	0.31	0.01	0.03	0.27	94	379
<i>aqua regia extractable part of trace elements (ng m⁻³)</i>								
Al	<13.9	<13.9	<46.4	<46.4	58.1	88.6	n.a.	>25
V	1.00	1.43	2.07	0.74	1.10	1.55	43	49
Cr	<0.75	<0.75	<0.75	<0.75	<2.51	<0.75	n.a.	n.a.
Mn	1.02	1.26	2.19	<0.80	0.86	1.18	24	>8
Fe	<23.3	26.6	55.2	<23.3	<23.3	30.0	>14	n.a.
Co	<0.049	0.050	0.076	<0.049	<0.049	0.055	>2	n.a.
Ni	<1.88	<1.88	2.12	<1.88	<1.88	<1.88	n.a.	n.a.
Cu	4.47	5.92	4.58	1.79	8.31	<1.56	32	364
Zn	<11.4	<11.4	19.9	<11.4	<11.4	<11.4	n.a.	n.a.
Rb	<0.16	<0.53	<0.53	<0.16	<0.16	<0.16	n.a.	n.a.
Sr	<0.33	<0.33	<0.33	<1.09	<1.09	<1.09	n.a.	n.a.
Mo	<0.42	0.45	0.69	<0.42	<0.42	<0.42	>7	n.a.
Cd	<0.11	0.12	0.17	<0.11	<0.11	<0.11	>9	n.a.
Sn	<1.35	1.39	1.69	<0.40	<1.35	<0.40	>3	n.a.
Sb	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Pb	3.70	2.99	4.14	<1.10	1.31	1.63	-19	>19
<i>water-soluble part of trace elements (ng m⁻³)</i>								

Al	<0.51	<1.72	<1.72	<1.72	<1.72	1.91	n.a.	n.a.
V	0.90	1.15	1.84	0.75	0.90	1.21	28	20
Cr	<0.21	<0.21	<0.72	<0.72	<0.72	<0.21	n.a.	n.a.
Mn	<0.38	0.39	1.58	<0.38	<0.38	0.53	>3	n.a.
Fe	1.47	2.50	12.6	1.77	1.56	4.15	70	-12
Co	0.019	0.021	0.058	0.019	0.018	0.035	13	-4
Ni	0.53	0.63	1.29	0.54	0.64	0.65	19	18
Cu	1.86	3.71	2.12	1.61	6.07	0.94	99	277
Zn	5.50	7.18	18.8	1.27	2.50	3.96	31	96
Rb	0.09	0.11	0.19	0.041	0.044	0.065	26	8
Sr	0.08	0.08	0.22	0.19	0.35	0.23	4	83
Mo	<0.34	<0.34	0.61	<0.34	<0.34	<0.34	n.a.	n.a.
Cd	<0.11	<0.11	0.12	<0.032	<0.11	<0.11	n.a.	n.a.
Sn	<0.18	<0.18	0.19	<0.18	<0.18	<0.18	n.a.	n.a.
Sb	0.31	0.39	0.66	0.23	0.25	0.32	23	12
Pb	0.13	0.13	0.76	0.19	0.18	0.28	2	-6

n.a. = not applicable

^a indoor 2 is related to indoor 1

Fig. A.1. Location of the sampling sites in Europe. The number of the investigated office buildings is also indicated on the map.



Fig. A.2. Scatter plot for the sum of the molar concentrations of the water-soluble cations multiplied with their corresponding charge and the sum calculated for the water-soluble anions.

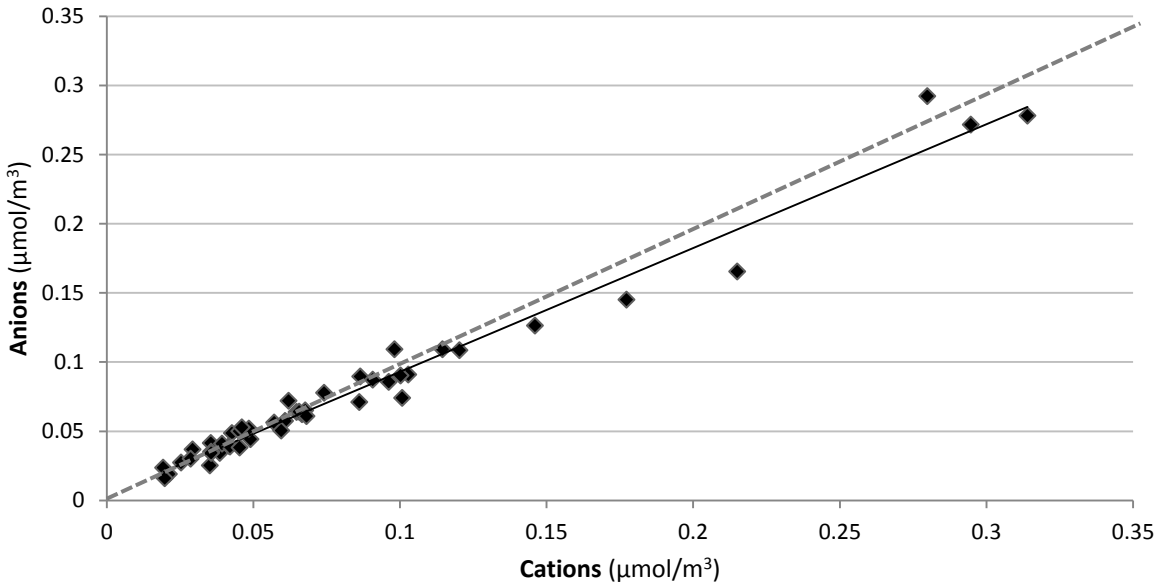


Fig. A.3. Ratios of indoor and outdoor trace element concentration values obtained for *aqua regia* extractions. Concentration is expressed in ng m^{-3} (a) and $\mu\text{g g}^{-1}$ (b). Inner squares in each box correspond to the mean value. The bottom, middle and top of each box correspond to the 25th, 50th and 75th percentile while whiskers indicate 10th and 90th percentiles. Individual outliers are also shown. Data lower than LOD was rejected from the calculation.

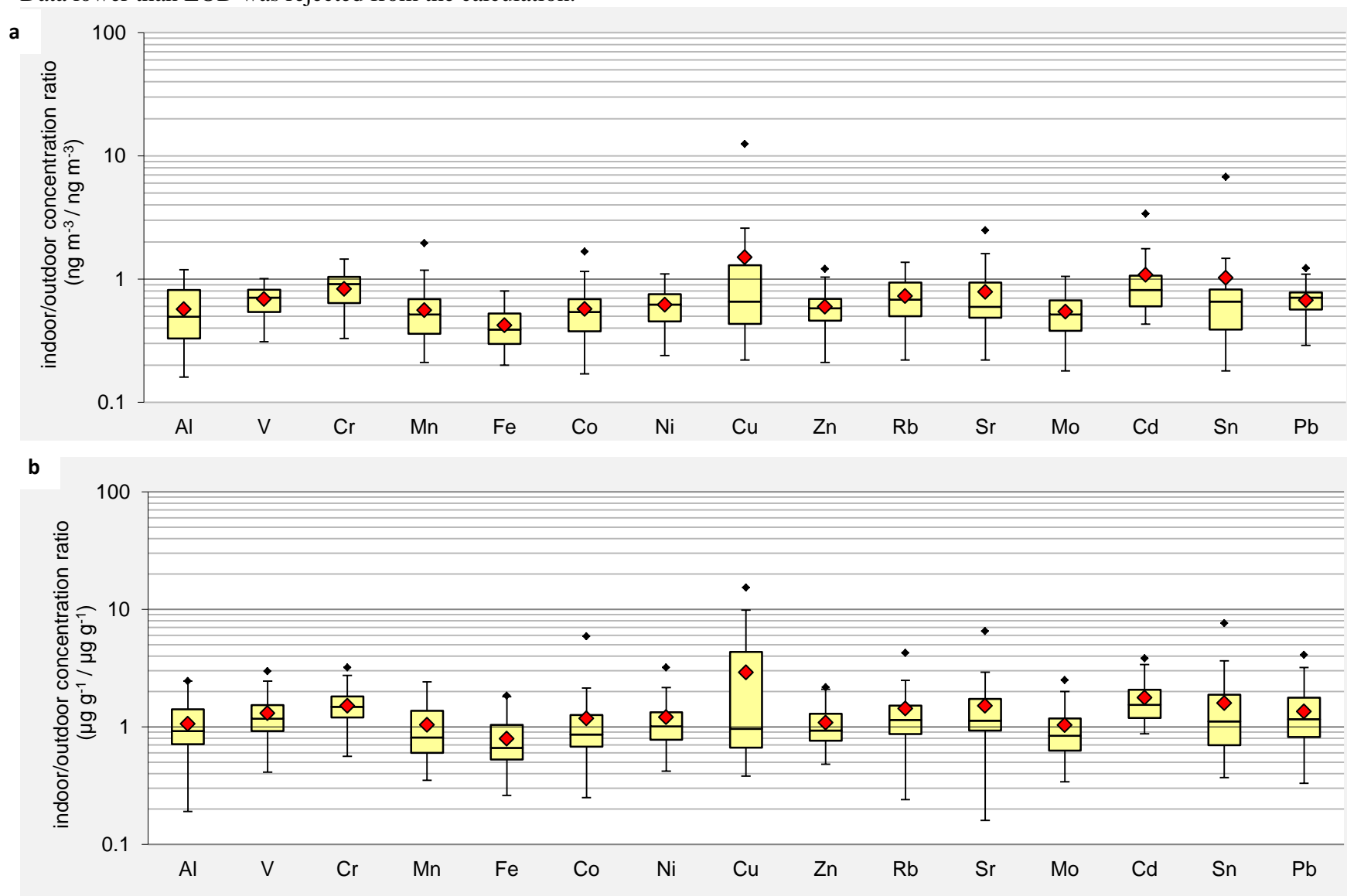


Fig. A.4. Ratios of trace element concentrations obtained for water and *aqua regia* extractions for the PM_{2.5} samples collected in Greece (a), The Netherlands (b) and Italy (c). Inner squares in each box correspond to the mean value. The bottom, middle and top of each box correspond to the 25th, 50th and 75th percentile while whiskers indicate 10th and 90th percentiles. Individual outliers are also shown. Data lower than LOD was rejected from the calculation.

