

Supplementary of

Highly time-resolved measurements of element concentrations in PM₁₀ and PM_{2.5}: Comparison of Delhi, Beijing, London, and Krakow

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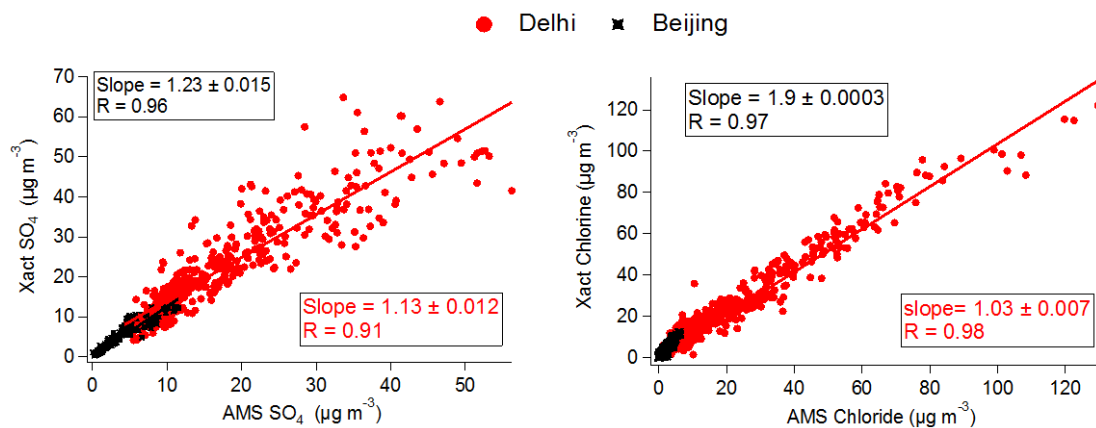
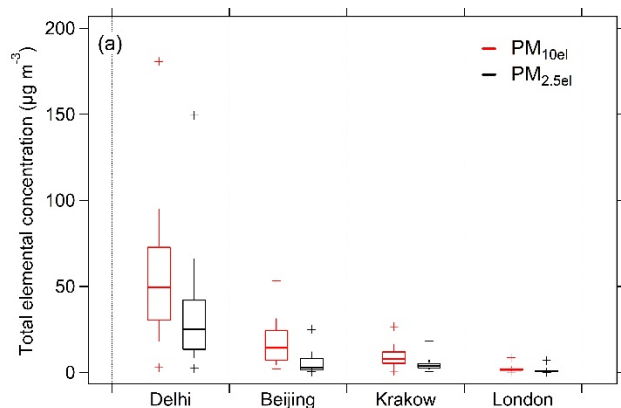


Figure S1: Comparison of Xact PM_{2.5} sulfate (3×S, assuming that all S occurred in the form of sulfate.) vs AMS sulfate (left) and Xact PM_{2.5} Cl vs AMS chloride (right) at Delhi (red; AMS PM₁) and Beijing (black; AMS PM_{2.5}) sites.



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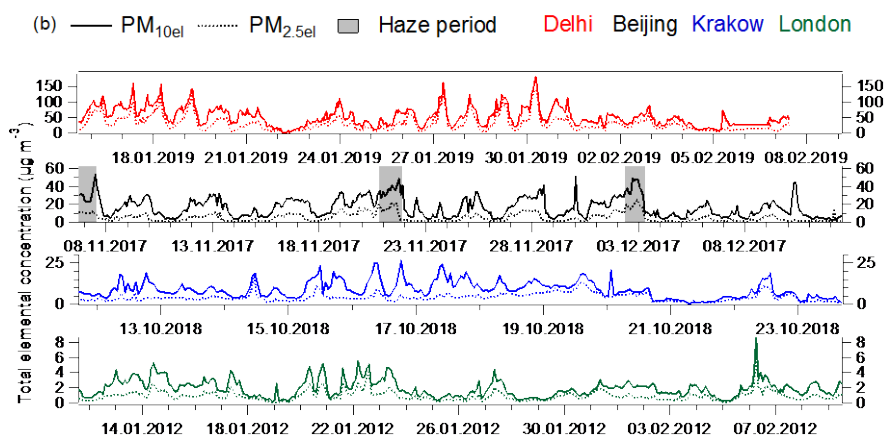


Figure S2: (a) Box-Whisker plots (top to bottom: maximum-p90-p75-p50-p25-p10-minimum) of total PM_{10el} and PM_{2.5el} concentrations and (b) Time series of hourly PM_{10el} and PM_{2.5el} at Delhi, Beijing, Krakow, and London.

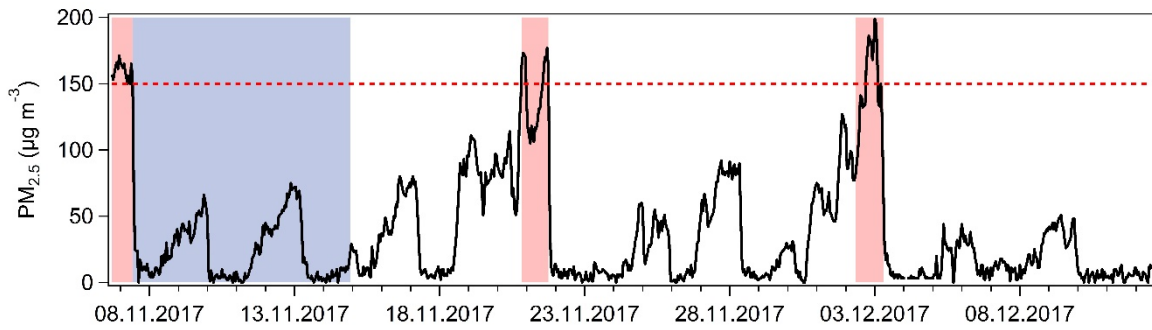


Figure S3: Time series of $PM_{2.5}$ total mass concentration in Beijing measured at the nearest national monitoring network station in Haidian District (2.5 km away from the Xact sampling site). The periods highlighted with a blue background relate to the non-heating period, while the rest belongs to the heating period. The red background colors represent haze events based on $PM_{2.5}$ concentrations $\geq 150 \mu\text{g m}^{-3}$ with a dashed red line, whereas the remaining periods are called non-haze.

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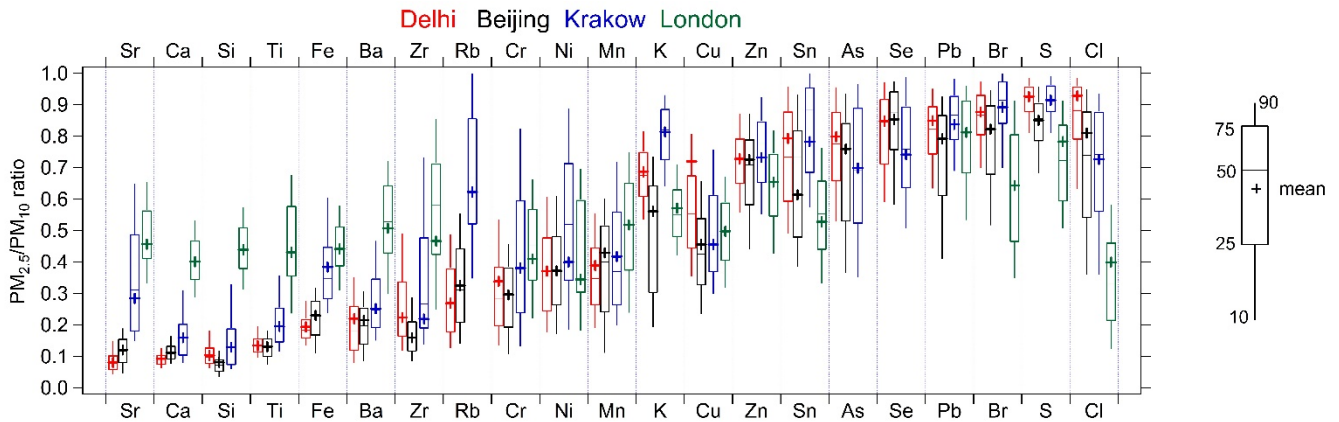
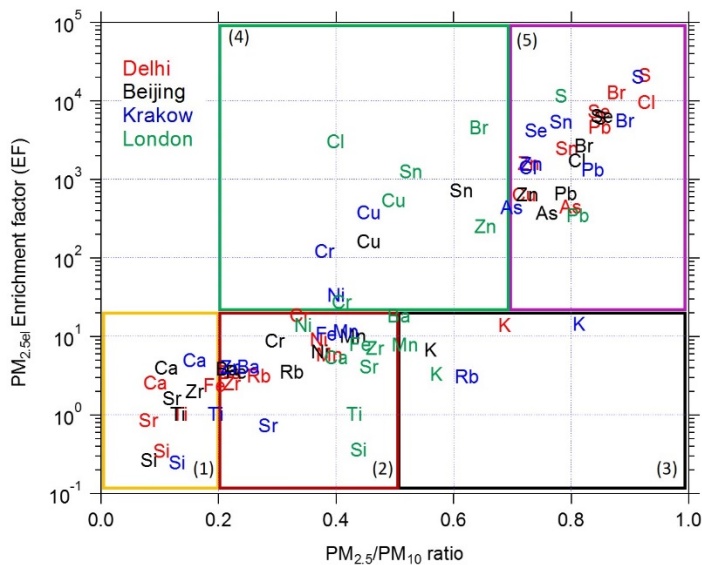
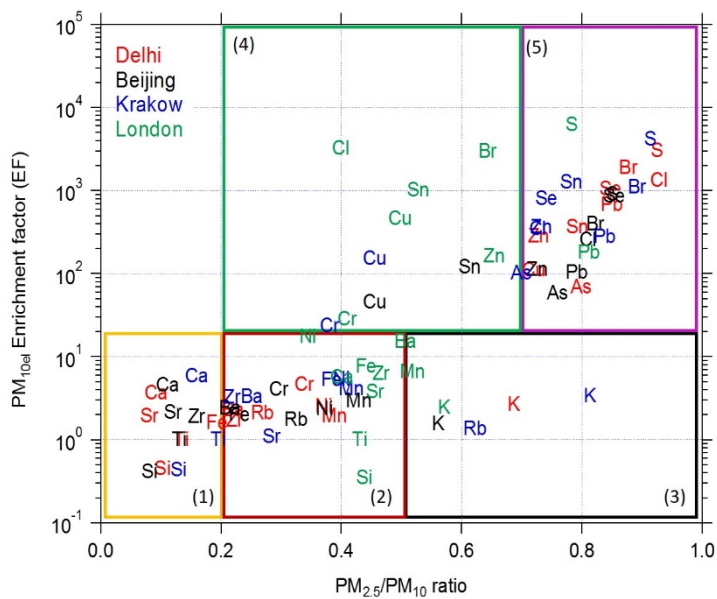


Figure S4: Box-whisker plot of the measured elemental $PM_{2.5}/PM_{10}$ ratios at all four sites. Box: First to third quartile range, -: median line, +: mean, whiskers: 10-90% percentiles. Note that Rb, As and Se were not measured in London. London measurements should be interpreted with caution due to uncertainties in the low size cut-off of the RDI, as discussed in Section 2.2.

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5 **Figure S5: Enrichment factors (EF) vs $PM_{2.5}/PM_{10}$ ratios at all four sites. The upper graph is for PM_{10ef} EF vs $PM_{2.5}/PM_{10}$ and the lower graph is for $PM_{2.5ef}$ EF vs $PM_{2.5}/PM_{10}$. Note that Rb, As and Se were not measured in London. London measurements should be interpreted with caution (especially with respect to the $PM_{2.5}/PM_{10}$ ratio) due to uncertainties in the low size cut-off of the RDI, as discussed in Section 2.2.**

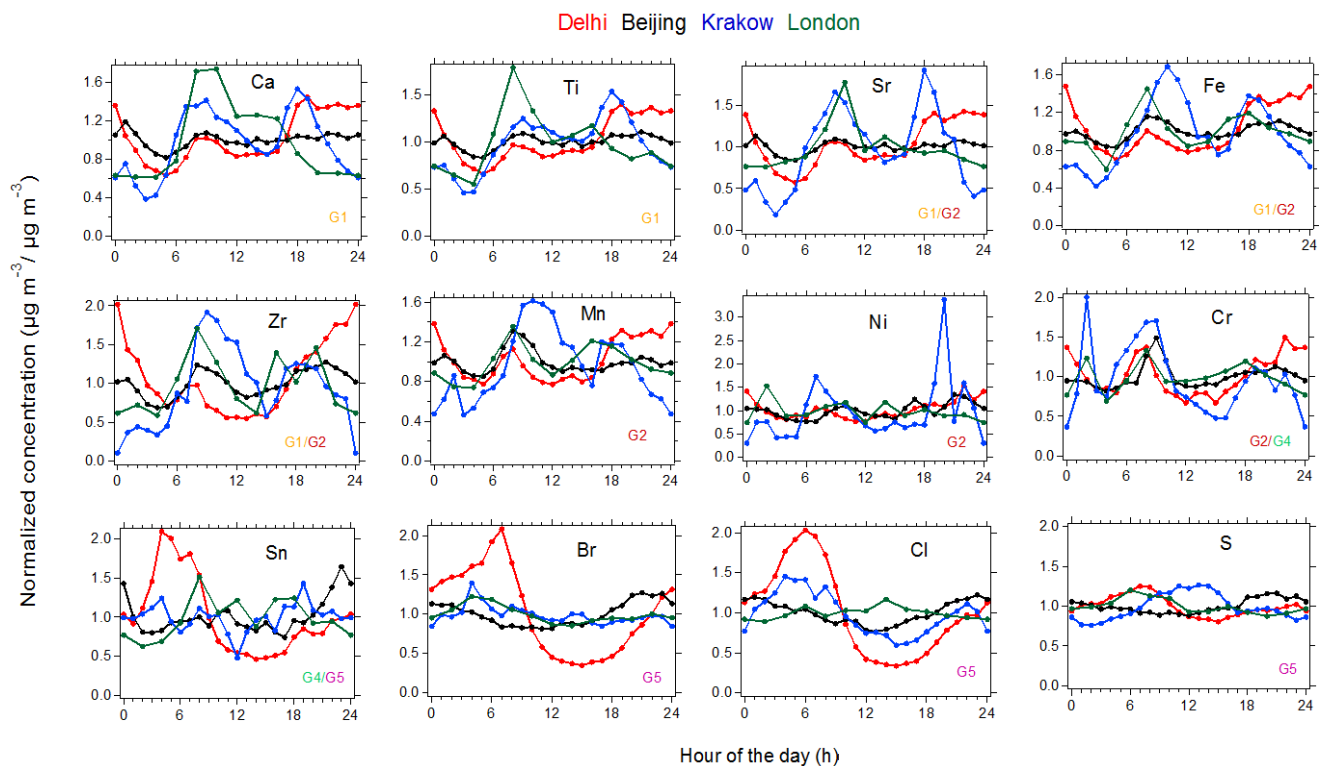
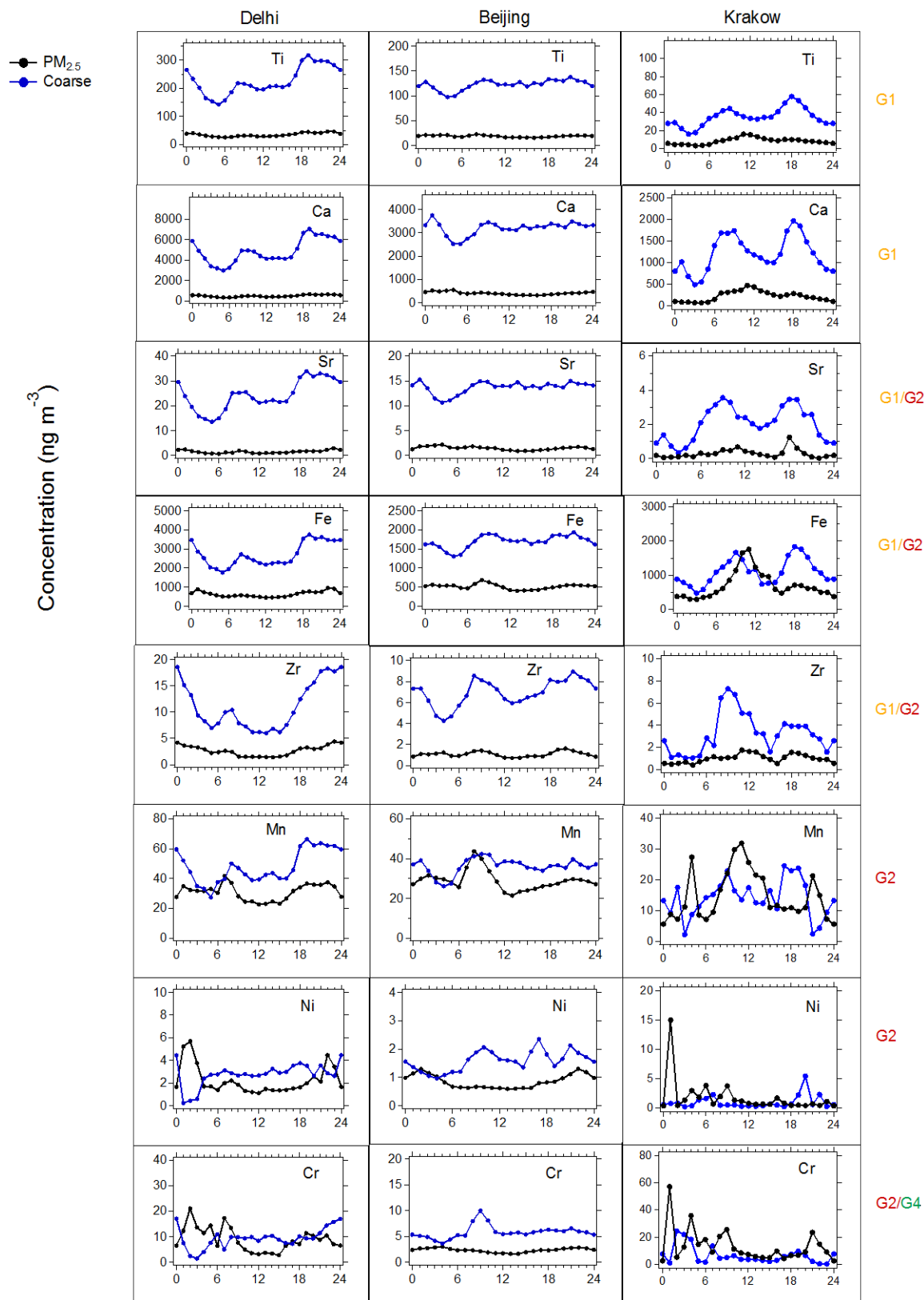


Figure S6: Diurnal patterns (mean) of elements in each group (G1: Group 1, G2: group 2, G3: Group 3, G4: Group 4, G5: Group 5) in PM₁₀ normalized by the mean values of the elements in PM₁₀ at Delhi, Beijing, Krakow, and London. Note that due to the time resolution of the original data the London data are 2-hour averages, while the other data are one-hour averages.



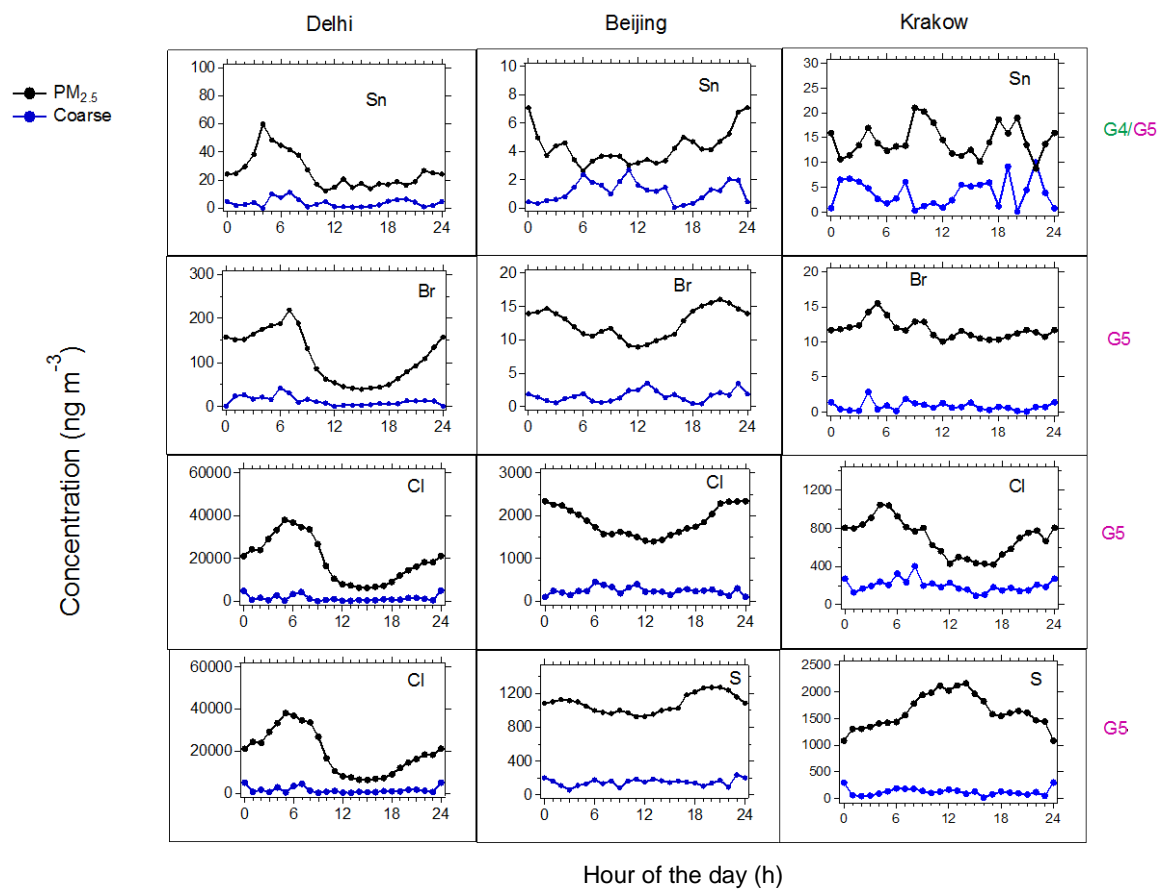


Figure S7: Diurnal patterns (mean) of elements in PM_{2.5} and coarse size fractions (PM₁₀-PM_{2.5}) at Delhi, Beijing, and Krakow, in each group (G1: Group 1, G2: group 2, G3: Group 3, G4: Group 4, G5: Group 5).

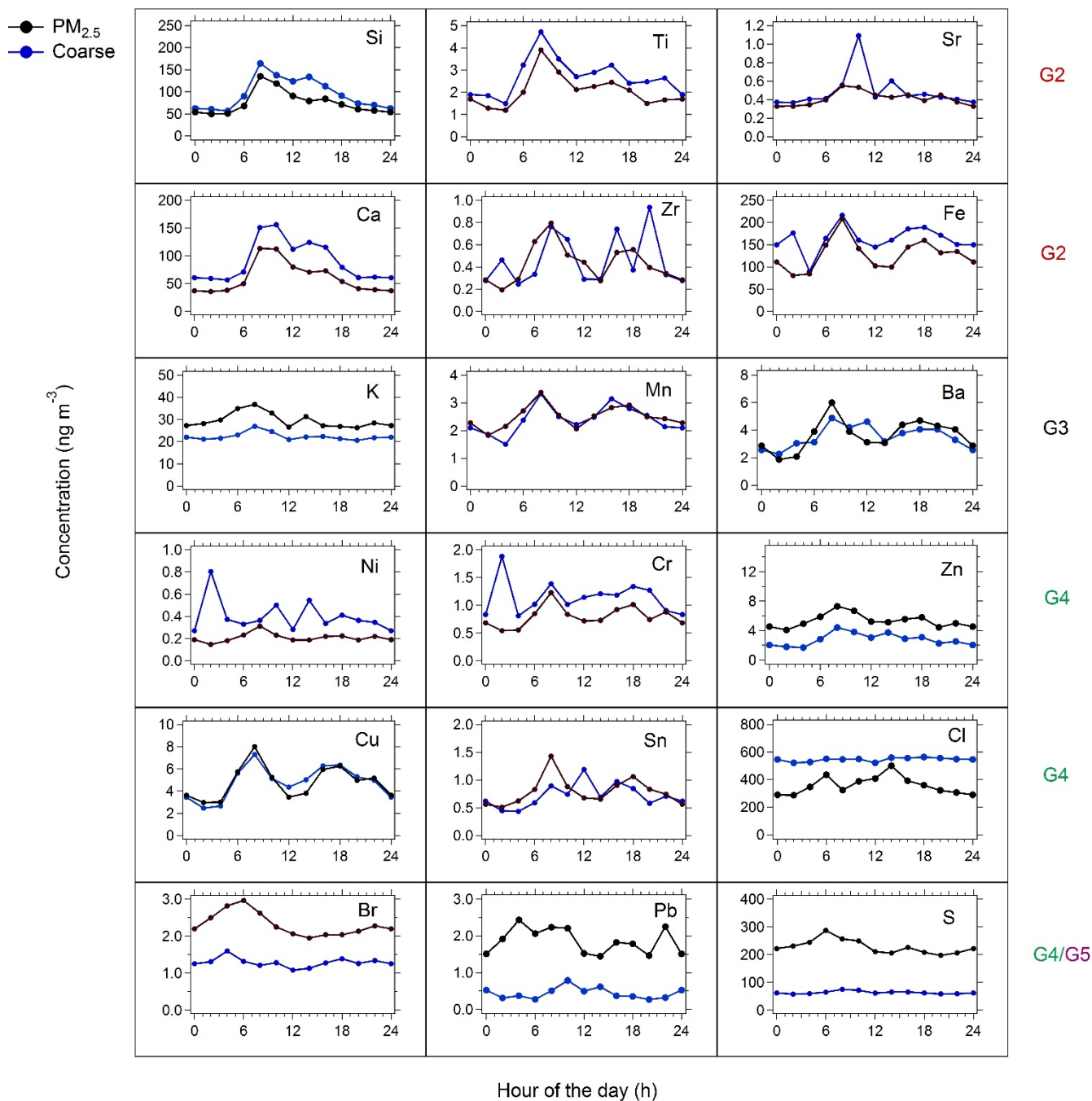


Figure S8: Diurnal patterns (mean) of elements in $PM_{2.5}$ and coarse size fractions ($PM_{10}-PM_{2.5}$) at London, in each group (G2: group 2, G3: Group 3, G4: Group 4, G5: Group 5). Note that Group 1 is absent in London. Note that due to the time resolution of the original data of London, hour of the day on the x-axis represents 2-hour averages. London measurements should be interpreted with caution due to uncertainties in the low size cut-off of the RDI, as discussed in Section 2.2.

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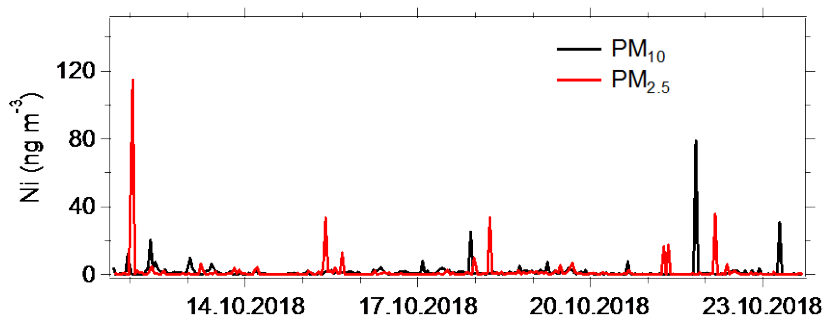
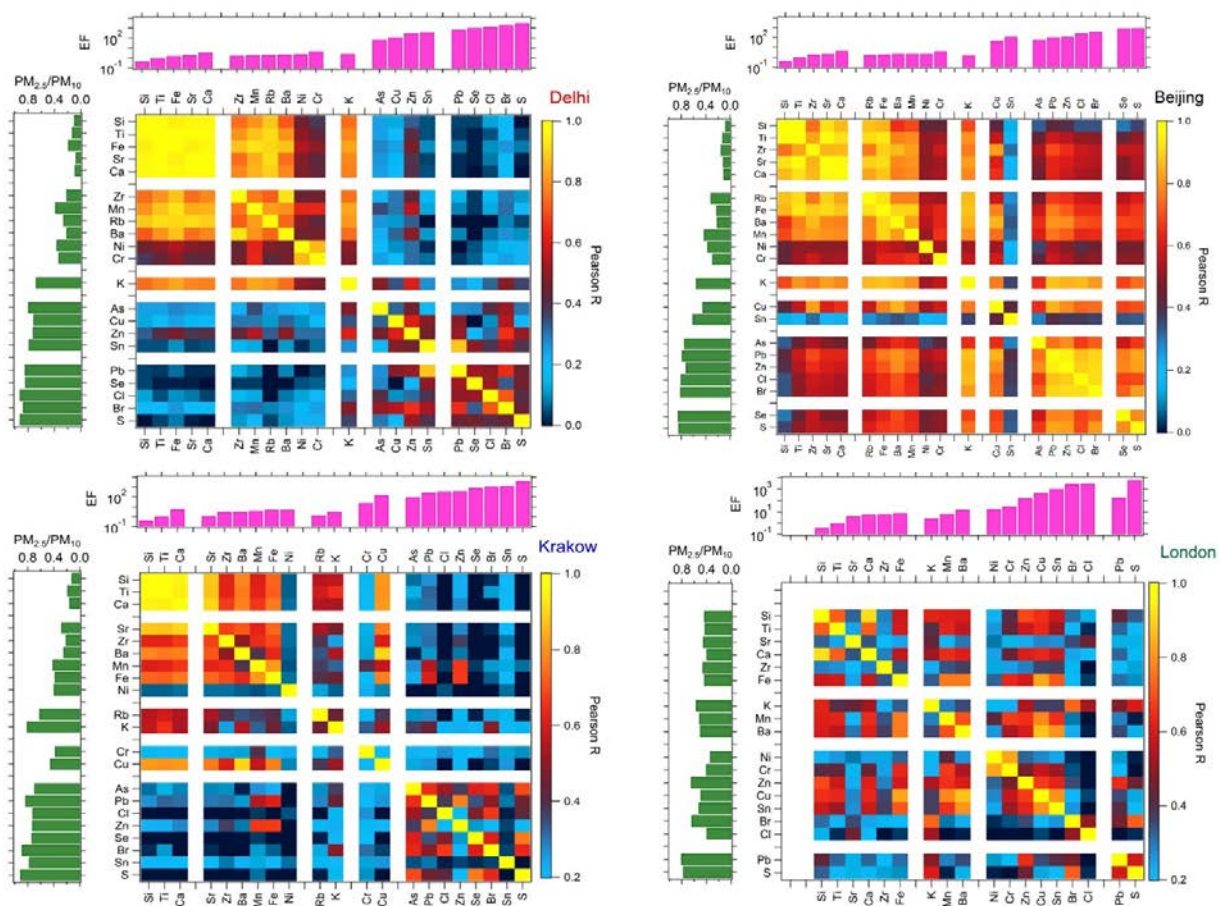


Figure S9: Time series of Ni in PM₁₀ (black) and PM_{2.5} (red) in Krakow.



5 Figure S10: Correlation (Pearson's *R*) matrix of measured elements in elemental PM₁₀ at all four sites (white color represents gap between each group elements). Elements are sorted by group along each axis. Note that in London, Group 1 (represented as white gap) is absent as well as Rb, As and Se were not measured. London measurements should be interpreted with caution due to uncertainties in the low size cut-off of the RDI, as discussed in Section 2.2.

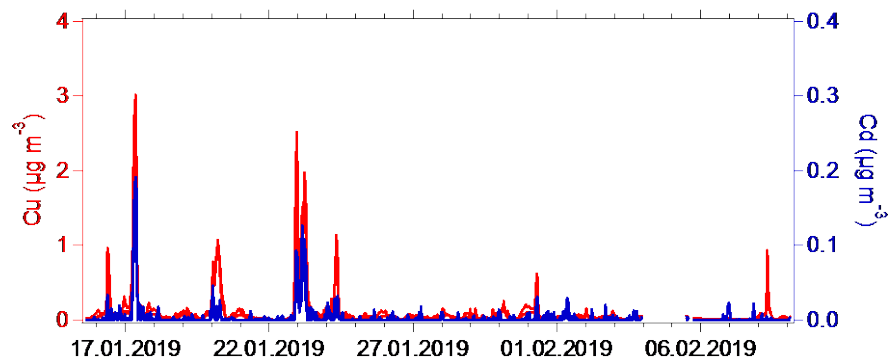
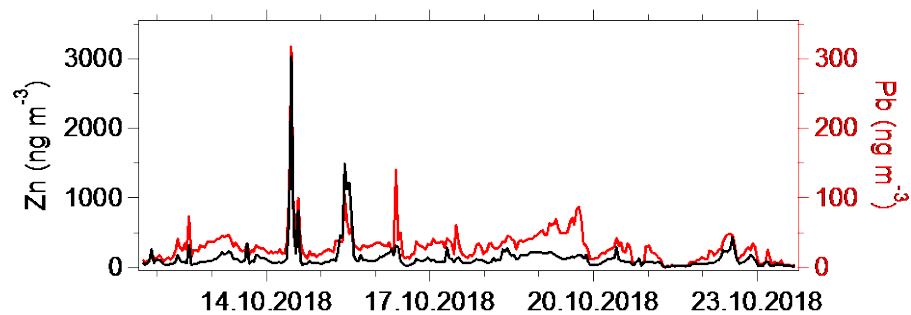


Figure S11: Time series of PM_{2.5} Cu and Cd in Delhi.



5 Figure S12: Time series of PM_{2.5} Zn and Pb in Krakow.

Table S1: Xact 625i minimum detection limits (MDL) of elements with 30 min and 60 min time resolution. The percentage of data points below MDL is reported for both sizes in Delhi, Beijing and Krakow.

| Element | Xact MDL | | Data points below MDL (%) | | | | | |
|---------|---------------------------------|---------------------------------|---------------------------|-------------------|------------------|-------------------|------------------|-------------------|
| | 60 min (ng m ⁻³) | 30 min (ng m ⁻³) | Delhi | | Beijing | | Krakow | |
| | | | PM ₁₀ | PM _{2.5} | PM ₁₀ | PM _{2.5} | PM ₁₀ | PM _{2.5} |
| Al | 170 | 500 | 18.8 | 61.4 | 24.5 | 86.1 | 86.9 | 99.3 |
| Si | 30.9 | 88.9 | 0 | 3.52 | 0 | 2.43 | 12.06 | 55.67 |
| P | 9.0 | 26.0 | 100 | 100 | 100 | 100 | 100 | 100 |
| S | 5.5 | 15.7 | 0 | 0 | 0 | 0 | 0 | 0 |
| Cl | 3.0 | 8.6 | 0 | 0 | 0 | 0 | 0 | 0 |
| K | 2.0 | 5.8 | 0 | 0 | 0 | 0 | 0 | 0 |
| Ca | 0.52 | 1.5 | 0 | 0 | 0 | 0.24 | 0 | 0 |
| Ti | 0.28 | 0.79 | 0 | 0 | 0 | 0.24 | 0.35 | 7.09 |
| V | 0.21 | 0.60 | 4.9 | 45.4 | 12.6 | 85.9 | 84.8 | 94.7 |
| Cr | 0.20 | 0.58 | 0 | 10.8 | 0.49 | 16.3 | 10.6 | 17.0 |
| Mn | 0.25 | 0.71 | 0 | 0 | 0 | 0 | 5.3 | 11.0 |
| Fe | 0.30 | 0.85 | 0 | 0 | 0 | 0.49 | 0 | 0 |
| Co | 0.24 | 0.68 | 98.8 | 96.9 | 93.4 | 98.1 | 98.6 | 100 |
| Ni | 0.17 | 0.47 | 3.5 | 27.0 | 5.8 | 30.2 | 39.0 | 58.9 |
| Cu | 0.14 | 0.39 | 0 | 0 | 0 | 0 | 0.35 | 0.35 |
| Zn | 0.12 | 0.33 | 0 | 0 | 0 | 0.24 | 0 | 0 |
| Ga | 0.10 | 0.29 | 99.6 | 100 | 68.0 | 83.5 | 99.6 | 99.3 |
| Ge | 0.10 | 0.28 | 99.8 | 100 | 82.3 | 81.0 | 98.2 | 98.2 |
| As | 0.11 | 0.31 | 0.20 | 100 | 0.73 | 4.1 | 6.4 | 10.3 |
| Se | 0.14 | 0.40 | 6.4 | 7.0 | 40.3 | 44.5 | 59.2 | 59.6 |
| Br | 0.18 | 0.52 | 0 | 0 | 0 | 0.73 | 0 | 0.35 |
| Rb | 0.33 | 0.95 | 10.9 | 57.7 | 9.0 | 47.0 | 65.6 | 86.5 |
| Sr | 0.38 | 1.1 | 2.9 | 56.2 | 0 | 42.6 | 46.1 | 91.8 |
| Y | 0.48 | 1.4 | 95.1 | 97.8 | 86.4 | 98.5 | 98.2 | 99.3 |
| Zr | 0.57 | 1.6 | 7.0 | 45.6 | 5.6 | 47.4 | 40.8 | 71.6 |
| Cd | 4.4 | 12.4 | 92.8 | 94.7 | 99.8 | 99.3 | 99.3 | 99.6 |
| In | 5.4 | 15.4 | 93.2 | 91.6 | 97.3 | 98.1 | 100 | 99.3 |
| Sn | 7.1 | 20.1 | 50.2 | 54.4 | 70.1 | 79.1 | 64.9 | 69.9 |
| Sb | 9.0 | 25.5 | 74.6 | 76.7 | 89.6 | 95.1 | 89.0 | 89.7 |
| Ba | 0.67 | 1.9 | 5.1 | 36.8 | 0.5 | 24.6 | 16.0 | 53.9 |
| Hg | 0.21 | 0.60 | 100 | 100 | 100 | 100 | 100 | 100 |
| Tl | 0.20 | 0.57 | 94.7 | 99.2 | 99.0 | 99.4 | 100 | 100 |
| Pb | 0.22 | 0.63 | 0 | 0 | 0 | 0.49 | 1.77 | 0.71 |
| Bi | 0.23 | 0.64 | 99.8 | 99.8 | 94.2 | 95.1 | 100 | 100 |

Table S2: Means, medians and 25–75th percentiles of PM₁₀ and PM_{2.5} concentrations (ng m⁻³) in Delhi, Beijing, Krakow and London (*BDL: below detection limit).

| Element | PM ₁₀ | | | | PM _{2.5} | | | |
|----------------|------------------|--------|------|-------|-------------------|--------|------|-------|
| | mean | median | q25 | q75 | mean | median | q25 | q75 |
| Delhi | | | | | | | | |
| Al | 3089 | 2593 | 919 | 4609 | 742 | 199 | BDL | 1055 |
| Si | 12158 | 10988 | 7428 | 16101 | 1241 | 1182 | 687 | 1721 |
| S | 7664 | 6411 | 4203 | 10320 | 7098 | 6060 | 3919 | 9454 |
| Cl | 20254 | 13104 | 5100 | 25989 | 19057 | 12183 | 4515 | 25126 |
| K | 3056 | 2609 | 1807 | 3834 | 2098 | 1743 | 1099 | 2678 |
| Ca | 5373 | 4686 | 3074 | 7227 | 494 | 408 | 259 | 643 |
| Ti | 262 | 238 | 163 | 343 | 35.1 | 30.5 | 20.4 | 44.7 |
| V | 5.9 | 5.1 | 3.1 | 8.3 | 1.29 | 0.78 | 0.00 | 1.96 |
| Cr | 17.4 | 12.2 | 7.2 | 23.7 | 9.1 | 3.5 | 1.42 | 8.5 |
| Mn | 79.3 | 64.4 | 42.2 | 99.6 | 31.5 | 20.8 | 12.6 | 37.7 |
| Fe | 3345 | 2932 | 1993 | 4281 | 648 | 500 | 355 | 725 |
| Ni | 4.9 | 3.9 | 2.4 | 6.5 | 2.3 | 1.12 | 0.4 | 2.3 |
| Cu | 128 | 47.8 | 25.0 | 91.1 | 96.1 | 27.4 | 13.0 | 54.2 |
| Zn | 784 | 606 | 379 | 1015 | 580 | 445 | 258 | 760 |
| As | 13.6 | 11.7 | 7.3 | 17.1 | 11.5 | 10.0 | 6.1 | 15.2 |
| Se | 3.9 | 3.0 | 1.50 | 4.6 | 3.5 | 2.8 | 1.42 | 4.2 |
| Br | 124 | 77.0 | 39.4 | 160 | 111 | 66.3 | 34.5 | 147 |
| Rb | 7.2 | 6.2 | 2.9 | 10.2 | 1.41 | 0.58 | BDL | 2.2 |
| Sr | 25.6 | 22.5 | 13.8 | 35.4 | 1.47 | 0.80 | BDL | 2.3 |
| Zr | 13.5 | 9.9 | 5.3 | 18.1 | 2.6 | 1.89 | 0.57 | 3.6 |
| Sn | 29.7 | 19.9 | 12.2 | 34.8 | 26.8 | 18.0 | 9.7 | 32.2 |
| Sb | 23.5 | 14.1 | 3.7 | 26.5 | 18.4 | 12.8 | 2.2 | 25.0 |
| Ba | 58.7 | 42.7 | 20.3 | 77.6 | 11.8 | 4.8 | 0.16 | 15.0 |
| Pb | 475 | 216 | 106 | 415 | 421 | 181 | 88.8 | 363 |
| Beijing | | | | | | | | |
| Al | 1524 | 1161 | 184 | 2478 | 68.4 | BDL | BDL | BDL |
| Si | 6060 | 5605 | 2866 | 7910 | 511 | 400 | 163 | 650 |
| S | 1224 | 708 | 445 | 1354 | 1084 | 578 | 376 | 1161 |
| Cl | 2089 | 684 | 203 | 3135 | 1841 | 479 | 134 | 2727 |
| K | 963 | 732 | 324 | 1533 | 546 | 265 | 100 | 906 |
| Ca | 3598 | 3239 | 1543 | 5234 | 414 | 342 | 174 | 592 |
| Ti | 141 | 128 | 67.9 | 195 | 18.8 | 15.6 | 7 | 26.3 |
| V | 1.98 | 1.54 | 0.65 | 2.7 | 0.11 | BDL | BDL | BDL |
| Cr | 8.2 | 7.2 | 3.1 | 11.6 | 2.4 | 1.73 | 0.41 | 3.9 |
| Mn | 65.0 | 55.8 | 25.2 | 94.5 | 29.0 | 20.3 | 6.4 | 44.2 |
| Fe | 2206 | 1946 | 981 | 3201 | 517 | 387 | 165 | 752 |
| Ni | 2.4 | 2.0 | 0.88 | 3.4 | 0.86 | 0.60 | 0.10 | 1.29 |
| Cu | 28.2 | 21.9 | 8.7 | 43.0 | 13.2 | 9.2 | 3.2 | 20.3 |
| Zn | 165 | 93.5 | 36.4 | 261 | 124 | 69.0 | 21.8 | 200 |
| As | 6.2 | 2.8 | 1.22 | 8.1 | 5.2 | 1.90 | 0.76 | 7.0 |
| Se | 1.7 | 0.36 | BDL | 2.5 | 1.67 | 0.25 | BDL | 2.4 |
| Br | 14.0 | 5.1 | 2.1 | 20.7 | 12.5 | 5.08 | 1.62 | 18.1 |
| Rb | 3.2 | 2.7 | 1.13 | 4.8 | 0.85 | 0.42 | BDL | 1.3 |
| Sr | 15.1 | 13.5 | 6.4 | 21.6 | 1.50 | 0.64 | BDL | 2.5 |
| Zr | 8.1 | 6.9 | 2.5 | 11.7 | 1.10 | 0.66 | 0.05 | 1.7 |
| Sn | 5.3 | 4.1 | 0.83 | 7.8 | 4.2 | 2.8 | BDL | 6.2 |
| Sb | 2.7 | 0.03 | BDL | 4.7 | 1.89 | BDL | BDL | 2.6 |
| Ba | 33.1 | 28.2 | 10.8 | 50.3 | 6.9 | 4.0 | 0.68 | 11.1 |
| Pb | 38.8 | 19.7 | 7.4 | 62.8 | 32.7 | 15.2 | 5.2 | 54.7 |

| Element | PM ₁₀ | | | | PM _{2.5} | | | |
|---------|------------------|--------|------|------|-------------------|--------|------|------|
| | mean | median | q25 | q75 | mean | median | q25 | q75 |
| Krakow | | | | | | | | |
| Al | 146 | BDL | BDL | BDL | 28 | BDL | BDL | BDL |
| Si | 1982 | 1461 | 385 | 2867 | 219 | 69.5 | 14.2 | 312 |
| S | 1780 | 1194 | 873 | 1931 | 1662 | 1099 | 801 | 1833 |
| Cl | 882 | 628 | 286 | 1103 | 688 | 431 | 195 | 857 |
| K | 653 | 641 | 440 | 885 | 534 | 506 | 344 | 718 |
| Ca | 1460 | 1059 | 459 | 1968 | 234 | 127 | 64.5 | 329 |
| Ti | 44.2 | 36.5 | 18.1 | 64.5 | 8.6 | 6.7 | 3.2 | 12.6 |
| V | 0.25 | BDL | BDL | 0.17 | 0.10 | BDL | BDL | BDL |
| Cr | 14.9 | 7.7 | 2.7 | 17.6 | 14.7 | 3.8 | 1.01 | 11.9 |
| Mn | 28.3 | 21.8 | 9.6 | 36.5 | 15.2 | 8.1 | 4.0 | 17.3 |
| Fe | 1833 | 1484 | 713 | 2437 | 722 | 521 | 252 | 879 |
| Ni | 1.73 | 0.73 | 0.24 | 1.72 | 2.1 | 0.36 | BDL | 0.94 |
| Cu | 29.4 | 22.0 | 12.0 | 40.7 | 14.0 | 10.9 | 5.9 | 19.2 |
| Zn | 168 | 129 | 76.9 | 191 | 140 | 91.4 | 60.9 | 150 |
| As | 3.3 | 3.1 | 1.95 | 4.4 | 2.8 | 2.5 | 1.19 | 3.6 |
| Se | 0.50 | 0.23 | BDL | 0.79 | 0.50 | 0.27 | BDL | 0.74 |
| Br | 12.2 | 10.6 | 6.2 | 15.3 | 11.7 | 9.8 | 5.8 | 15.0 |
| Rb | 0.79 | 0.50 | BDL | 1.30 | 0.34 | BDL | BDL | 0.55 |
| Sr | 2.4 | 1.39 | BDL | 3.66 | 0.31 | BDL | BDL | 0.16 |
| Zr | 4.3 | 2.3 | 0.77 | 5.61 | 1.04 | 0.66 | BDL | 1.71 |
| Sn | 17.4 | 15.5 | 7.9 | 24.6 | 14.3 | 12.1 | 4.3 | 22.7 |
| Sb | 10.8 | 8.7 | 1.19 | 16.7 | 10.0 | 6.4 | BDL | 17.1 |
| Ba | 14.3 | 10.5 | 2.1 | 20.3 | 3.4 | 1.59 | BDL | 4.9 |
| Pb | 32.7 | 30.9 | 18.2 | 41.5 | 29.5 | 25.8 | 15.7 | 36.7 |
| London | | | | | | | | |
| Al | 96.1 | 82.2 | 59.5 | 121 | 45.8 | 42.7 | 29.3 | 54.8 |
| Si | 174 | 140 | 77 | 225 | 76.4 | 58.2 | 35.8 | 104 |
| S | 292 | 213 | 136 | 322 | 229 | 139 | 81.4 | 258 |
| Cl | 908 | 626 | 226 | 1391 | 362 | 162 | 57.2 | 483 |
| K | 52.1 | 47.8 | 30.0 | 69.0 | 29.7 | 25.5 | 15.6 | 38.9 |
| Ca | 154 | 114 | 72.2 | 195 | 61.8 | 45.5 | 26.9 | 79.1 |
| Ti | 4.8 | 3.4 | 1.87 | 6.2 | 2.1 | 1.52 | 0.75 | 2.8 |
| V | 1.18 | 0.83 | 0.52 | 1.42 | 0.56 | 0.43 | 0.25 | 0.72 |
| Cr | 1.97 | 1.37 | 0.72 | 2.5 | 0.81 | 0.62 | 0.31 | 1.03 |
| Mn | 4.9 | 3.8 | 2.3 | 5.8 | 2.5 | 1.96 | 0.98 | 3.0 |
| Fe | 293 | 216 | 130 | 362 | 129 | 92.2 | 51.6 | 161 |
| Ni | 0.62 | 0.35 | 0.18 | 0.70 | 0.21 | 0.16 | 0.08 | 0.28 |
| Cu | 9.8 | 7.2 | 4.0 | 12.2 | 4.9 | 3.1 | 1.84 | 6.0 |
| Zn | 8.2 | 6.0 | 2.7 | 11.3 | 5.4 | 3.5 | 1.69 | 7.9 |
| Br | 3.6 | 3.2 | 1.76 | 4.9 | 2.3 | 1.73 | 1.03 | 2.8 |
| Sr | 0.92 | 0.75 | 0.47 | 1.16 | 0.42 | 0.34 | 0.21 | 0.53 |
| Zr | 0.91 | 0.46 | 0.20 | 1.07 | 0.44 | 0.26 | 0.12 | 0.52 |
| Sn | 1.53 | 1.07 | 0.52 | 1.87 | 0.81 | 0.55 | 0.27 | 1.04 |
| Sb | 1.18 | 0.84 | 0.43 | 1.44 | 0.63 | 0.42 | 0.22 | 0.81 |
| Ba | 7.3 | 4.9 | 2.7 | 8.6 | 3.7 | 2.4 | 1.33 | 4.6 |
| Pb | 2.3 | 1.31 | 0.63 | 2.8 | 1.89 | 1.0 | 0.45 | 2.3 |

Table S3: Relative fractions (%) of elements in both sizes for all four sites.

| Element | Delhi | | Beijing | | Krakow | | London | |
|---------|------------------|-------------------|------------------|-------------------|------------------|-------------------|------------------|-------------------|
| | PM ₁₀ | PM _{2.5} | PM ₁₀ | PM _{2.5} | PM ₁₀ | PM _{2.5} | PM ₁₀ | PM _{2.5} |
| Si | 22.6 | 3.9 | 36.4 | 9.9 | 22.1 | 5.1 | 9.1 | 8.4 |
| S | 14.2 | 22.2 | 7.3 | 21.0 | 19.9 | 38.5 | 15.2 | 25.0 |
| Cl | 37.6 | 59.6 | 12.5 | 35.7 | 9.8 | 16.0 | 47.3 | 39.7 |
| K | 5.7 | 6.6 | 5.8 | 10.6 | 7.3 | 12.4 | 2.7 | 3.3 |
| Ca | 10.0 | 1.55 | 21.6 | 8.0 | 16.3 | 5.4 | 8.0 | 6.8 |
| Ti | 0.49 | 0.11 | 0.85 | 0.36 | 0.49 | 0.20 | 0.25 | 0.23 |
| Cr | 0.03 | 0.03 | 0.05 | 0.05 | 0.17 | 0.34 | 0.10 | 0.09 |
| Mn | 0.15 | 0.10 | 0.39 | 0.56 | 0.32 | 0.35 | 0.26 | 0.28 |
| Fe | 6.2 | 2.0 | 13.2 | 10.0 | 20.5 | 16.7 | 15.2 | 14.1 |
| Ni | 0.01 | 0.01 | 0.01 | 0.02 | 0.02 | 0.05 | 0.03 | 0.02 |
| Cu | 0.24 | 0.30 | 0.17 | 0.26 | 0.33 | 0.32 | 0.51 | 0.53 |
| Zn | 1.45 | 1.81 | 0.99 | 2.4 | 1.88 | 3.2 | 0.43 | 0.59 |
| Br | 0.23 | 0.35 | 0.08 | 0.24 | 0.14 | 0.27 | 0.19 | 0.25 |
| Sr | 0.05 | 0 | 0.09 | 0.03 | 0.03 | 0.01 | 0.05 | 0.05 |
| Zr | 0.03 | 0.01 | 0.05 | 0.02 | 0.05 | 0.02 | 0.05 | 0.05 |
| Sn | 0.06 | 0.08 | 0.03 | 0.08 | 0.19 | 0.33 | 0.08 | 0.09 |
| Ba | 0.11 | 0.04 | 0.20 | 0.13 | 0.16 | 0.08 | 0.38 | 0.40 |
| Pb | 0.88 | 1.32 | 0.23 | 0.63 | 0.36 | 0.68 | 0.12 | 0.21 |