

Figure S1. Map with the location of measurements site, the red mark corresponds to 39° 58' 28" North, 116° 22' 15" East.

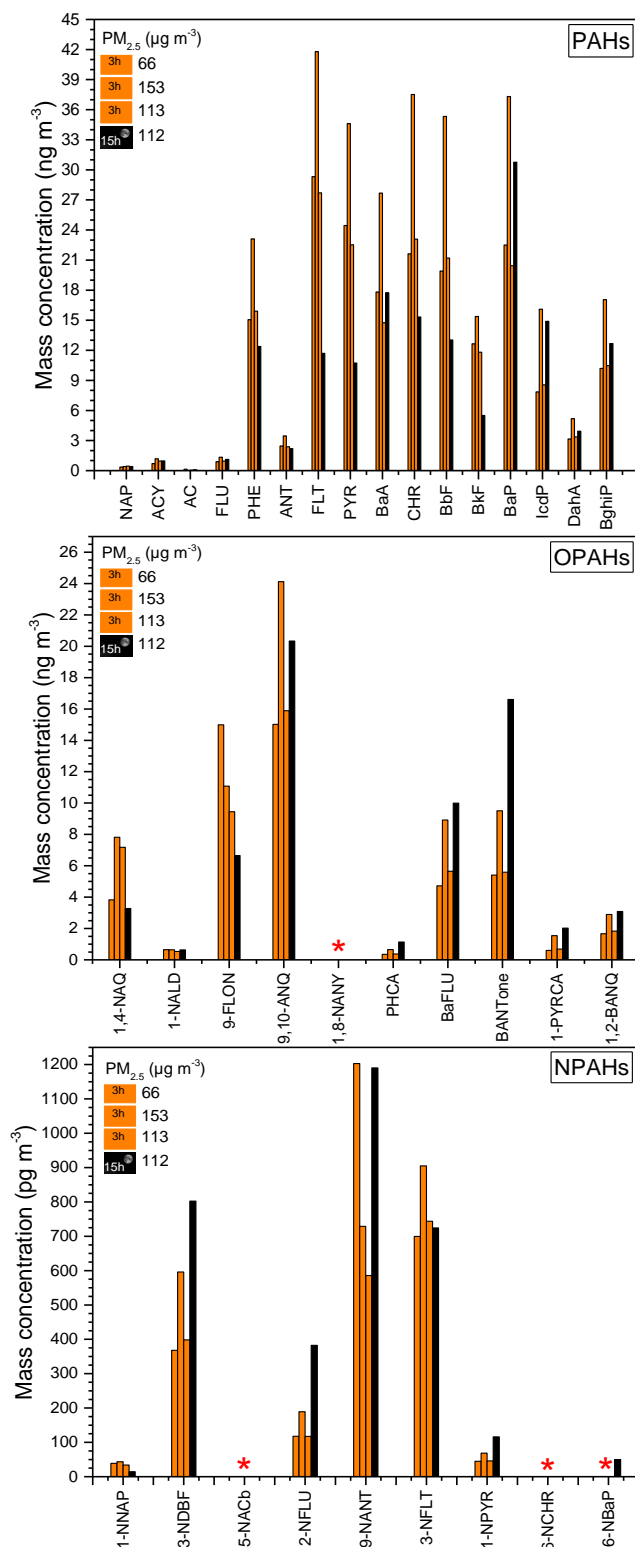


Figure S2. Column distribution illustrating the highest concentrations recorded during the sampling campaign (29 Nov 2016) for individual 16PAHs, 10OPAHS and 9NPAHs in the 3 h (day) and 15 h (night) samples. The first 3 h (PM_{2.5} 130) correspond to the first sampled filter at 8:30 in the morning and so forth. Asterisk (*) means below LOQ except for 1,8-NANY, it means outside the dynamic range.

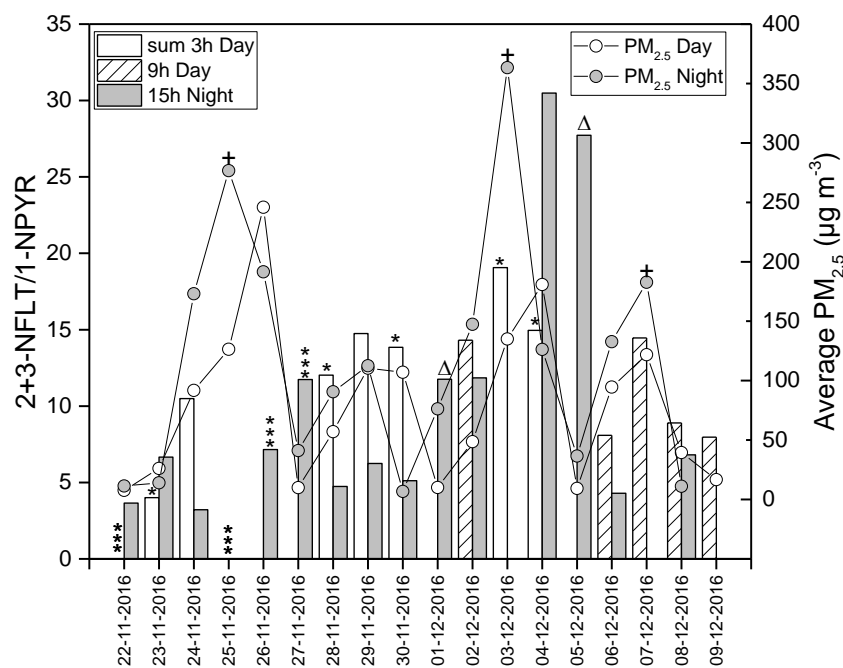


Figure S3. Ratio of 2+3-Nitrofluoranthene/1-Nitropyrene in $PM_{2.5}$ during daytime and night-time samples. One asterisk (*) means 1-NPYR < LOQ in one sample of 3 h, hence the ratios are overestimated; three asterisk mean below LOQ in three samples of 3 h (daytime data not available); (Δ) symbols refer to 1-NPYR < LOQ in the 9 h day samples (daytime data not available); (+) symbols mean night-time data not available.

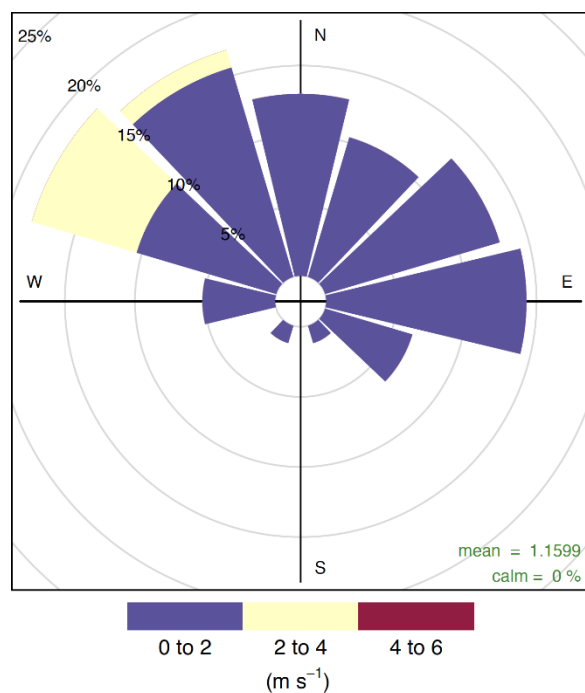


Figure S4. Wind-rose plot for the period from 22 November 2016 to 9 December 2017 in Beijing.

| | Time | Σ PAHs | Σ OPAHs | Σ NPAHs |
|-----------------|------|---------------|----------------|----------------|
| O ₃ | 3 h | -0.60 | -0.59 | -0.47 |
| | 9 h | -0.78 | -0.85 | -0.80 |
| | 15 h | -0.79 | -0.64 | -0.75 |
| CO | 3 h | 0.60 | 0.62 | 0.44 |
| | 9 h | 0.90 | 0.92 | 0.92 |
| | 15 h | 0.88 | 0.86 | 0.56 |
| NO | 3 h | 0.60 | 0.55 | 0.38 |
| | 9 h | 0.97 | 0.98 | 0.98 |
| | 15 h | 0.84 | 0.73 | 0.37 |
| NO ₂ | 3 h | 0.48 | 0.58 | 0.43 |
| | 9 h | 0.84 | 0.89 | 0.90 |
| | 15 h | 0.87 | 0.82 | 0.68 |
| SO ₂ | 3 h | 0.72 | 0.74 | 0.59 |
| | 9 h | 0.90 | 0.89 | 0.90 |
| | 15 h | 0.85 | 0.86 | 0.58 |
| HONO | 3 h | 0.87 | 0.94 | 0.94 |
| | 9 h | 0.95 | 0.87 | 0.88 |
| | 15 h | 0.85 | 0.77 | 0.52 |
| T° | 3 h | 0.04 | 0.18 | 0.07 |
| | 9 h | -0.17 | -0.23 | -0.20 |
| | 15 h | 0.09 | 0.07 | 0.16 |
| RH | 3 h | 0.73 | 0.71 | 0.59 |
| | 9 h | 0.66 | 0.59 | 0.63 |
| | 15 h | 0.50 | 0.58 | 0.34 |

Table S1. Pearson correlation coefficients between Σ PAHs, Σ OPAHs, Σ NPAHs and O₃, CO, NO, NO₂, SO₂, HONO, temperature and relative humidity during the daytime (18 days with 3 h and 9 h sampling time) and night-time (14 nights with 15 h sampling time). Strong positive correlation (0.8-1) are shown in Bold (P<0.05).

| | Time | n | HONO | P value |
|---------|-------------|-----------|-------------|------------------|
| | 3 h | 15 | 0.94 | <0.001 |
| 1-NNAP | 9 h | 5 | 0.82 | >0.05 |
| | 15 h | 10 | 0.59 | >0.05 |
| | 3 h | 15 | 0.93 | <0.001 |
| 3-NDBF* | 9 h | 5 | 0.82 | >0.05 |
| | 15 h | 10 | 0.66 | <0.05 |
| | 3 h | 1 | NA | |
| 5-NAC | 9 h | 0 | NA | |
| | 15 h | 4 | 0.89 | >0.05 |
| | 3 h | 16 | 0.92 | <0.001 |
| 2-NFLU | 9 h | 5 | 0.84 | >0.05 |
| | 15 h | 10 | 0.83 | <0.01 |
| | 3 h | 16 | 0.90 | <0.001 |
| 9-NANT* | 9 h | 5 | 0.78 | >0.05 |
| | 15 h | 10 | 0.15 | >0.05 |
| | 3 h | 13 | 0.93 | <0.001 |
| 3-NFLT* | 9 h | 5 | 0.98 | <0.01 |
| | 15 h | 10 | 0.65 | <0.05 |
| | 3 h | 6 | 0.90 | <0.01 |
| 1-NPYR | 9 h | 4 | 0.81 | >0.05 |
| | 15 h | 9 | 0.94 | <0.001 |
| | 3 h | 1 | NA | |
| 6-NCHR | 9 h | 0 | NA | |
| | 15 h | 2 | NA | |
| | 3 h | 0 | NA | |
| 6-NBaP | 9 h | 1 | NA | |
| | 15 h | 6 | 0.3 | >0.05 |

* Major compounds in NPAHs
(NA) not available.

Table S2. Pearson correlation coefficients between individual NPAHs in PM_{2.5} and HONO. (n) correspond to the number of data in common between each NPAHs and HONO concentrations. Values in Bold correspond to strong correlation with high significance levels (R=0.8-1; P<0.05, 95% level of confidence).

| Compound | TEF | References |
|-----------------------------|--------|-------------------------|
| PAHs | | |
| Napthalene | 0.001 | Nisbet and Lagoy., 1992 |
| Acenaphthylene | 0.001 | Nisbet and Lagoy., 1992 |
| Acenaphthene | 0.001 | Nisbet and Lagoy., 1992 |
| Fluorene | 0.0005 | Hester et al., 1998 |
| Phenanthrene | 0.0005 | Hester et al., 1998 |
| Anthracene | 0.0005 | Hester et al., 1998 |
| Fluoranthene | 0.05 | Hester et al., 1998 |
| Pyrene | 0.001 | Hester et al., 1998 |
| Benzo[a]anthracene | 0.082 | Durnant et al., 1996 |
| Chrysene | 0.017 | Durnant et al., 1996 |
| Benzo[b]fluoranthene | 0.25 | Durnant et al., 1996 |
| Benzo[k]fluoranthene | 0.11 | Durnant et al., 1996 |
| Benzo[a]pyrene | 1 | OEHHA., 1994 |
| Indeno[1,2,3-cd]pyrene | 0.1 | Hester et al., 1998 |
| Dibenzo[a,h]anthracene | 1.1 | Hester et al., 1998 |
| Benzo[g,h,i]perylene | 0.02 | Hester et al., 1998 |
| OPAHs | | |
| 7H-Benz[de]anthracene-7-one | 0.0039 | Durnant et al., 1996 |
| Nitro-PAHs | | |
| 5-Nitroacenaphthene | 0.01 | OEHHA., 1994 |
| 2-Nitrofluorene | 0.01 | OEHHA., 1994 |
| 9-Nitroanthracene | 0.0032 | Durnant et al., 1996 |
| 3-Nitrofluoranthene | 0.0026 | Durnant et al., 1996 |
| 1-Nitropyrene | 0.1 | OEHHA., 1994 |
| 6-Nitrochrysene | 10 | OEHHA., 1994 |

Table S3. Toxicity Equivalency Factor (TEFs) for individual PAHs, OPAHs and Nitro-PAHs.