

3 Results and discussion

3.1 Physicochemical characteristics and spatial distribution of Ba-containing particles

3.1.1 Temporal variations of Ba mass concentration and Ba-containing particle counts

Based on comprehensive observations from the four sites, fireworks were identified as the dominant aerosol source during the study period. During FI, Ba mass concentrations increased by 17- to 40-fold, while K^+ (9- to 23-fold), Cl^- (2- to 3-fold), and heavy metals such as Cu (2- to 14-fold) and Pb (2- to 3-fold) also rose simultaneously (Table 2, Figs. 1 and S4). $PM_{2.5}$ increased by 2- to 3-fold, while secondary inorganic ions (SO_4^{2-} and NO_3^-) showed smaller increases (1- to 3-fold), indicating active atmospheric aging (Peng et al., 2021). Notably, secondary inorganic ions and $PM_{2.5}$ during FII were lower than background levels ($FII/BII < 1$). The overall enhancements during FII were substantially smaller than those during FI, reflecting the brief duration of the Lantern Festival firework event rather than suppressed secondary formation. Therefore, the subsequent analysis focused primarily on FI, where the firework signals were most pronounced.

During the period when fireworks were permitted, air quality deteriorated sharply over a short timescale. Ba mass concentrations and Ba-containing particle counts exceeded background levels by approximately two orders of magnitude, with hourly peaks up to 1000-fold. This magnitude is comparable to that of severe firework events reported globally, such as Diwali celebrations in India (Kulshrestha et al., 2004; Tanda et al., 2019; Wang et al., 2007). These enhancements are substantially greater than the 4.5- to 40-fold increases documented in regions with stricter controls, consistent with findings by Huang et al. (2024).

Diurnal variations showed $PM_{2.5}$ mass concentration, Ba mass concentration, and Ba-containing particle counts rising sharply from evening, peaking at night (20:00–02:00 LT) at levels more than an order of magnitude above background, then dropping rapidly in early morning (Fig. 1b). This pattern is directly linked to nighttime fireworks practices. Particle size analysis revealed significant increases in the 0.1–2.0 μm range (Fig. 1c). In the 0.5–1.0 μm fraction, Ba-containing particle counts surged from 2193 during background to 24 624 during firework periods, underscoring the strong particle-generating capacity of fireworks in this size range. This pronounced increase in the 0.5–1.0 μm accumulation mode is consistent with previous findings that more than 80 % of firework-generated metals, including Ba, are concentrated in the submicrometric region ($< 1 \mu m$) (Crespo et al., 2012). A 6.7-fold increase in particle number concentration in the 0.5–1.0 μm range during Milan fireworks has been reported (Vecchi et al., 2008), which is lower than the 11.2-fold increase observed here, suggesting particularly intense firework emissions in this study.

3.1.2 Spatial heterogeneity across policy zones

The observed urban–rural gradient appears to be associated with regulatory measures and human activity intensity rather than simple downwind dispersion, and both $PM_{2.5}$ and Ba peak mass concentrations exhibited similar spatial patterns (Fig. 2). The highest concentration ($PM_{2.5}$: $89 \mu g m^{-3}$; Ba: $3411 ng m^{-3}$) occurred at PYDXC, a restricted-fireworks suburban area with high population density (5327 people km^{-2} ; Guangzhou Municipal Statistics Bureau, 2023). In contrast, the urban core site (GYQ), despite higher population density (28 400 people km^{-2} , 2023 data), exhibited lower peak concentrations. Concentrations at suburban NSPZ were slightly lower than the urban core, while the rural background site (CHLK) showed the lowest levels. This pattern suggests that regulatory policy (ban vs. restriction) is consistent with a possible influence on spatial heterogeneity of peak pollution during episodic events, although other factors such as local firework activity, enforcement intensity, meteorological conditions, atmospheric transport, and proximity to emission sources may also contribute (Kong et al., 2015). Thus, our interpretation should be considered preliminary and warrants verification with additional data (e.g., enforcement records and wind field analysis).

3.2 Mixing state and identification of early-aged and more aged particle types

3.2.1 Mixing state and chemical characteristics of Ba-containing particles

Figure 3a presents the mass spectra of two representative single particles, OCIN and N, which exhibited the most distinct chemical fingerprints among the four categories identified in Sect. 2.3. These two types were selected to illustrate the contrasting chemical features between particles with different mixing states, while the average mass spectra of the remaining types (NS and S) are provided in Fig. S3b. The OCIN particles are characterized by intense Ba^+ [m/z 138] and BaO^+ [m/z 156] signals in the positive ion spectrum, along with prominent Cl^- [m/z −35], O^- [m/z −16], and NO_3^- [m/z −62] peaks in the negative ion spectrum. In contrast, the N type particles exhibit a pronounced increase in the relative peak area of NO_3^- [m/z −62], while the Cl^- signal remains relatively unchanged. To quantify the distribution of these chemical types across the entire aerosol population, we examined the mixing states of all detected Ba-containing particles at the four sites during FI (Fig. 3b). The majority were internally mixed with nitrate (N type, 62.4 %), followed by particles mixed with both chloride and nitrate (OCIN type, 13.8 %), and those containing sulfate (NS and S types combined, 13.6 %TS1). Particles with other mixing states accounted for the remaining 10.2 %TS2. The temporal evolution of these particle types further reveals the aging process (Fig. 3c). During the early phase of FI, OCIN particles were more abundant with clear diurnal variations, while