

PM_{2.5} Chemical Composition Analysis

Preliminary Analysis

Steps

- Data Preprocessing
- Descriptive Statistics & Seasonal Comparison (XRF and IC)
- XRF and IC PCA Analysis
- Seasonal Chemistry Highlights
- Ionic Balance and Key Ratios
- Integrating XRF and IC Insights

XRF Analysis

Principal Component Analysis

PC	Explained Variance	Dominant Loadings	Interpretation
1	31.71%	S (0.93) , Zn (-0.87), Cl (-0.85), Al (-0.67), Fe (-0.64), Na (-0.66)	Secondary sulfate vs mixed anthropogenic metals — Strong S loading suggests secondary sulfate (from SO ₂ oxidation); Zn, Cl, Na, and Fe suggest contributions from waste burning, industrial metal emissions, and sea salt aerosol; PC1 contrasts sulfate formation against primary metal-rich sources.
2	19.83%	Ni (0.66) , Mg (0.64), Na (0.43), Al (-0.49), Si (-0.60), Fe (-0.49), K (-0.59)	Crustal dust vs industry-related Ni — Negative Al, Si, Fe, and K support crustal/soil dust; positive Ni and Mg suggest industrial/metal processing emissions possibly from nearby smelting or combustion activity.
3	14.46%	Ca (0.68) , Si (0.67), Mg (0.58), Ni (0.40)	Road dust and construction — Ca, Si, and Mg are common in construction materials and urban dust; also possibly from re-suspension of road dust.
4	8.56%	V (0.78) , Pb (0.32), NO	Combustion source: residual fuel oil and traffic — Vanadium is a tracer for heavy fuel oil combustion (e.g., shipping or industrial boilers); Pb may suggest traffic-related emissions or residual industrial combustion (though lower than historical due to unleaded fuel).

Seasonal Analysis (as mass ratio)

XRF

Element	Dry Mean	Wet Mean	P-value	Interpretation
S	54.36	30.56	0.0000	Secondary sulfate formation dominates in dry season, likely due to enhanced photochemistry and limited wet scavenging.
K	13.33	10.88	0.0006	Biomass burning tracer higher in dry season, consistent with regional burning and less rainfall.
Na	7.42	13.96	0.0000	Sea salt or marine aerosol signal higher in wet season, likely due to stronger monsoon winds and moisture.
Cl	0.97	4.99	0.0000	May reflect enhanced sea salt or waste burning emissions during wet season, though elevated Cl often co-occurs with Zn in informal waste burning.
Al, Ca, Fe (Crustal elements)	Al↑, Ca↑, Fe↑	All higher in wet season	<0.005	Suggest increased resuspension of soil/dust , possibly due to urban traffic on wet roads or wind-driven resuspension.
Zn	5.03	13.61	0.0000	Strong rise in wet season indicates waste burning, industrial, or vehicular emissions , often tied to informal urban combustion.
Pb	1.75	5.54	0.0000	Higher Pb in wet season suggests traffic or residual industrial combustion , despite unleaded fuel.
Ni	0.028	0.030	0.0453	Slight increase; industrial or oil combustion related, though marginal difference.
Mg	0.822	0.685	0.0021	Slightly higher in dry season; possible dust signal.
Si	4.78	5.13	0.1005	No significant seasonal difference.
V	0.024	0.029	0.2645	Not significantly different; V indicates residual fuel oil , but stable across seasons.

Anions-Cations Analysis

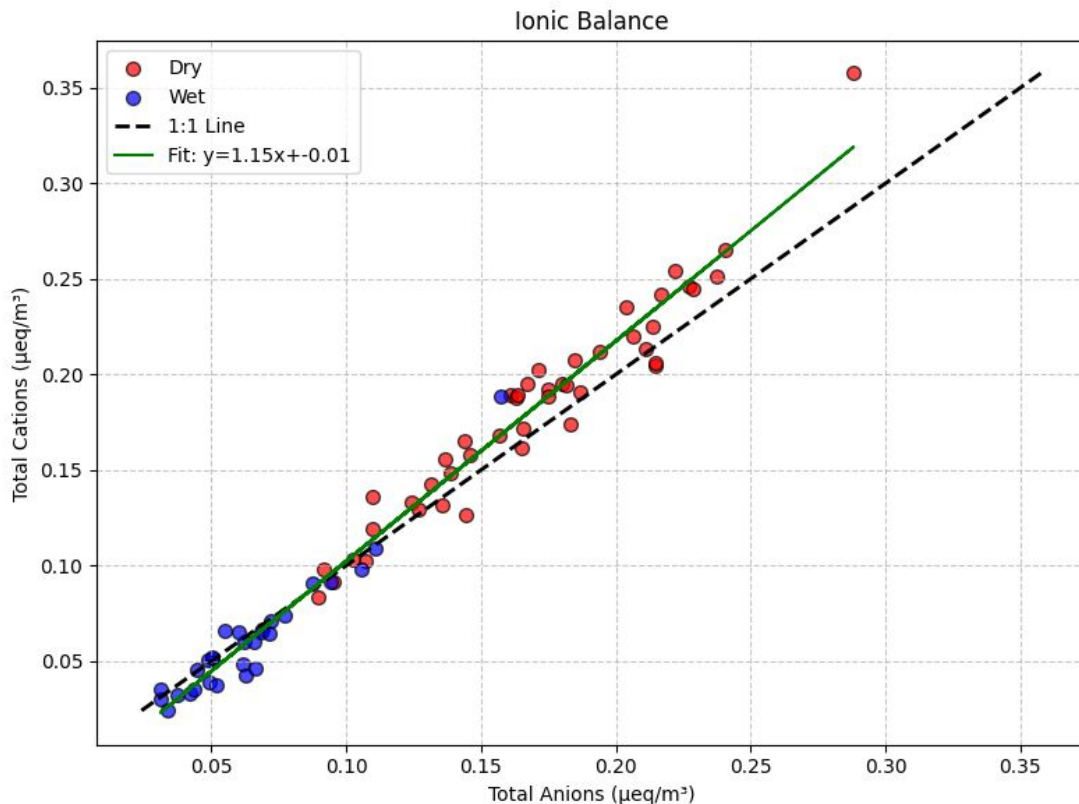
Principal Component Analysis

PC	Explained Variance	Dominant Loadings	Interpretation
1	43.10%	SO₄²⁻ (0.98) , NH ₄ ⁺ (0.96), K ⁺ (0.63), Ca ²⁺ (0.47), NO ₃ ⁻ (0.25)	Secondary inorganic aerosols (SIA) — Dominated by (NH₄)₂SO₄ formation; K ⁺ and Ca ²⁺ suggest mixed biomass burning or crustal contributions . This is the main component for photochemical sulfate episodes.
2	21.55%	Cl⁻ (0.88) , Na ⁺ (0.89), K ⁺ (0.60)	Sea salt influence and possible waste burning — High Na ⁺ and Cl ⁻ align with marine aerosol, while K ⁺ hints at possible chlorinated biomass or mixed combustion .
3	16.72%	NO₃⁻ (0.90) , NO ₃ ⁻ -N (0.87)	Nitrate aerosol formation — Likely NH₄NO₃ , which forms under cooler or humid conditions. Not dominant, but contributes to secondary PM fraction.
4	9.84%	Mg²⁺ (0.81) , Ca ²⁺ (0.43), Cl ⁻ (-0.30), K ⁺ (-0.31)	Crustal/resuspended dust signal — Mg ²⁺ and Ca ²⁺ suggest soil/road dust; Cl ⁻ and K ⁺ negative loadings could represent chemical depletion during transport or influence of acid-base reaction in the atmosphere.

Seasonal Analysis (in $\mu\text{g}/\text{m}^3$)

Ion	Dry Mean	Wet Mean	P-value	Interpretation
SO_4^{2-}	7.60	2.42	0.0000	Strongly elevated in dry season , indicating photochemical SO_2 oxidation and secondary sulfate aerosol formation under sunny, stagnant conditions.
NH_4^+	2.57	0.57	0.0000	Ammonium-rich neutralization of SO_4^{2-} , forming $(\text{NH}_4)_2\text{SO}_4$ in dry season. Drastic reduction in wet season due to dilution and washout.
Cl^-	0.03	0.27	0.0000	Significantly higher in wet season; likely from sea salt spray or chlorinated emissions (e.g., waste burning) under humid conditions.
K^+	0.56	0.32	0.0000	Higher in dry season, suggesting biomass burning or combustion activity (K^+ is a known tracer).
$\text{SO}_4\text{-S}$	2.54	0.81	0.0000	Sulfur from sulfate mirrors SO_4^{2-} trend—supports sulfate dominance in dry conditions.
$\text{NH}_4\text{-N}$	1.99	0.44	0.0000	Further confirms ammonium-based neutralization is more active in the dry season.
Mg^{2+}	0.033	0.028	0.0025	Slightly elevated in dry season; likely crustal or road dust origin.
Ca^{2+}	0.135	0.084	0.0051	Crustal material also more prominent in dry season, from soil resuspension or urban dust .
Na^+	0.319	0.345	0.0387	Slightly higher in wet season; could reflect marine air intrusion , though not dominant.
NO_3^-	0.511	0.385	0.6437	Not significantly different; nitrate less influenced by season , possibly due to local, short-lived formation or scavenging.

Ionic Balance Analysis



- **Interpretation:**
 - **Slope > 1 (1.15):** indicates a **slight excess of cations** over anions on average.
 - **Intercept ≈ -0.01 :** close to zero, suggesting **no major fixed offset** and good proportional scaling.

Slight cation excesses are typical in:

- Urban dust samples rich in crustal materials (Ca^{2+} , Mg^{2+}),
- Ammonium-rich environments where NH_4^+ may not be fully neutralized by SO_4^{2-} or NO_3^- .

$\text{SO}_4^{2-}/\text{NO}_3^-$ Ratio

The $\text{SO}_4^{2-}/\text{NO}_3^-$ ratios range from ~4.8 to over 12, consistently >1.

This indicates:

- **Dominance of sulfur-based secondary aerosol**, likely from **SO_2 emissions** (coal combustion, industrial activity).
- NO_3^- contributes less, suggesting either limited vehicular NO_x conversion or scavenging effects.
- The ratio also implies **longer-range transport** influence, as SO_4^{2-} is more stable and transported farther than NO_3^- .

NH_4^+ to $(\text{SO}_4^{2-} + \text{NO}_3^-)$ Ratio in Equivalents

The **neutralization ratio** ranges from **0.34 to 0.99**.

A **fully neutralized aerosol** (complete $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 formation) would yield a ratio ≈ 1 .

Interpretation:

- **Under-neutralization** indicates that some sulfate may exist as **acidic species (e.g., H_2SO_4)**.
- This is consistent with Southeast Asian urban aerosols during **dry seasons**, when **NH_3 is limited** or SO_2 is in excess.

Non-Sea-Salt Sulfate (nss-SO₄²⁻) and Potassium (nss-K⁺)

nss-SO₄²⁻ dominates total sulfate, often contributing >95% of the total (e.g., 3.07 of 3.11 µg/m³ in IND_A 001).

- Indicates **anthropogenic SO₂ origin** (power plants, vehicles, etc.).

nss-K⁺ is also the main portion of total K⁺.

- K⁺ from sea salt (0.037 × Na⁺) is minimal.
- High nss-K⁺ is a strong **biomass burning tracer**, supporting the PC1 interpretation from earlier PCA and dry season activity.

Methods Consistency

Does XRF sulfur (total S) correlate with IC sulfate (SO_4^{2-})?

Yes – strong and direct correlation

- **XRF S** has a **very strong loading in PC1 (0.93)**, which is the dominant component (31.7% variance).
- **IC SO_4^{2-} and SO_4^{2-} -S** both load **very strongly in PC1 (0.98)**, which explains 43.1% of the IC variance.
- Both PC1s represent **secondary sulfate aerosol**, likely from **SO_2 oxidation during photochemical activity**, dominant in the dry season.

Interpretation: These results reflect the same source — **secondary sulfate formation**, confirming that **XRF S and IC SO_4^{2-} track the same atmospheric processes.**

Does XRF potassium correlate with IC K⁺?

Yes – consistent cross-method signal

- **XRF K** has moderate positive loading in **PC1 (0.35)** and negative in **PC2 (–0.59)** of the XRF PCA, often interpreted as **biomass burning or mixed combustion**.
- **IC K⁺** has significant loading in **PC1 (0.63)** and **PC2 (0.60)** in the IC PCA.
- This suggests **IC K⁺ is influenced by both secondary aerosol (PC1) and sea salt/combustion processes (PC2)**.
- The variability in K across PCs implies **multiple sources** (e.g., **biomass burning, waste combustion, and coastal inputs**).

Interpretation: XRF and IC potassium both point to **biomass or mixed combustion sources**, with IC offering finer chemical resolution (e.g., separating ionic K⁺ from crustal K).

If crustal elements are high in XRF, is there any corresponding Ca^{2+} or Mg^{2+} in IC (beyond sea salt contributions)?

Yes – especially in PC4 of IC PCA

- In **XRF PCA**, crustal tracers like **Al, Si, Ca, Fe, Mg** load heavily in **PC2 and PC3**, associated with **dust or construction material**.
- In **IC PCA**, **Ca^{2+} and Mg^{2+}** show their strongest influence in:
 - **PC4**: Mg^{2+} (0.81), Ca^{2+} (0.43)
 - **Ca^{2+} also contributes to PC5** (0.71), separated from sea salt PCs.
- Importantly, **Na^+ and Cl^-** (sea salt) are isolated in **PC2**, indicating that PC4 reflects **non-marine crustal influence**.

Interpretation: Yes, crustal elements identified by XRF are **confirmed by IC Ca^{2+} and Mg^{2+}** , supporting the presence of **resuspended dust or mineral particles**, particularly during the dry season.