# ASAAQ 2005, 27-29 April 2005, San Francisco, California USA URBAN VS. RURAL AIR POLLUTION IN NORTHERN VIETNAM

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## Abstract

Air pollution affects not only the cities but also many rural areas of Vietnam, which has been experiencing a high rate of economic growth over the last years. The comparison of air pollution in urban and rural areas, therefore, will provide insights into the sources and properties of air pollutants, especially those affecting large areas in the region. For this purpose, air samples were collected concurrently at Hanoi (urban) and Lucnam (rural), about 65 km to the northeast. Samples were analyzed for black carbon, water-soluble ions and chemical elements to provide inputs for receptor modeling.

The mean coarse  $PM_{10}$  mass concentration (CM) at the urban site is 37.8 µg m<sup>-3</sup>, about two times higher than that at the rural site (19.1 µg m<sup>-3</sup>). The mean fine  $PM_{10}$  mass (FM) concentrations, however, are almost similar at the two sites (31 µg m<sup>-3</sup>). Positive Matrix Factorization (PMF) applied to aerosol chemical compositions derived six similar sources for the coarse fraction at both sites, namely soil dust incorporating sulphate and nitrate, soil dust containing soil organic matter and ammonium sulphate, coal fly ash from distant and local sources and marine aerosol. Traffic (road) dust was found only at the Hanoi site contributing 8% of the coarse mass. Vehicles, however, are the main contributor to coarse soil dust, which is about three times more abundant in Hanoi than in Lucnam. Coal-derived particles are slightly more abundant in Hanoi (16% of CM) than in Lucnam (36% of CM).

Six similar sources were found for fine particulates at the two sites, namely long-range transport (LRT), Cl-depleted marine aerosol, distant and local fly ash, soil dust and biomass burning. Again, vehicle emission was found only in Hanoi contributing 8% of FM. LRT is the largest source, accounting for 36% of FM at the two sites. Coal fly ash accounts for 30 and 37% of FM at the urban and rural site, respectively. Biomass burning is much stronger at the rural site (11% vs 6%).

Thus, urban and rural settings considerably differ by the abundance of the coarse fraction, reflecting the contrast in traffic and construction activities. The difference, however, is insignificant for the fine fraction as the impacts of LRT aerosols and coal fly ash are similar at the two sites. Furthermore, the contribution from vehicle emissions at the urban site is balanced by the stronger biomass burning emission at the rural site.

#### Keywords:

PIXE, Ion Chromatography, Positive Matrix Factorization, long range transport, sulphate, nitrate, ammonium.

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# 1. Introduction

Previous studies on air particulates in urban areas of Vietnam have shown that mineral dust (MD) consisting of soil and coal fly ash particles and long-range transport (LRT) aerosols containing ammonium sulphate dominate the coarse (PM<sub>2.2-10</sub>) and fine (PM<sub>2.2</sub>) PM<sub>10</sub> fractions, respectively (Hien et al., 2001, 2004). While LRT aerosols originate from regional and transboundary pollution sources, MD is derived from the local soils and coal burning.

In the cities, the major producers of soil dust are traffic and construction/road works, which have been expanding over the last years. In the meantime, coal is gradually replaced by gas and electricity for domestic cooking. The situation, however, is guite different in rural areas of northern Vietnam, where both traffic and construction works are sparse, while coal is increasingly used for domestic cooking and manufacturing of bricks, tiles, lime and pottery. Furthermore, major coal-burning sources, such as power, cement and chemical plants, are located away from the cities. Therefore, soil dust is expected to be less abundant in rural areas, but this may not be the case for coal fly ash. On the other hand, the LRT component is expected to be not much different at the two areas. Thus, a comparative receptor modeling study of coarse and fine  $PM_{10}$  at the urban and rural sites would give insights into the sources and properties of coarse and fine PM<sub>10</sub>.

#### 2. Site description

Hanoi, Vietnam's capital city of over 2 million people, is located in the Red River delta (21.02°N, 105.85°E), about 100 km west of the East China Sea and about 150 km to the borders with China and Laos (Fig. 1). Samples were collected at the meteorological garden, about 100 m away from a highway and 10 km from industrial zones in southern and northern suburban areas of Hanoi.



Figure 1. Map of northern Vietnam

Air samples were concurrently collected on the roof of a two-story house in a small village surrounded by a paddy field in Lucnam (21.18°N, 106.33°E), about 60 km east of Hanoi. This area can be regarded as free of traffic.

Meteorological conditions in Hanoi and Lucnam are controlled by the common monsoon regime, which is driven by cold air from the Siberia High in winter and humid hot air from the Highs over Pacific and Indian Oceans in summer (Hien et al., 2004). Meteorological parameters are routinely measured only at the Hanoi site.

#### 3. Sampling and sample analysis

Coarse and fine PM<sub>10</sub> were collected on two separate 47 mm diameter nuclepore polycarbonate filters using a Gent Stacked Filter Unit. A co-located sampling experiment showed that the two air samplers produce similar particulate mass concentrations within  $\pm 7\%$ .

Loaded filters were analyzed for watersoluble ions (WSI), black carbon (BC) and elemental components using lon Chromatography (IC), reflectance and Proton Induced X-ray Emission (PIXE) methods, respectively. The relative uncertainties of the concentrations were about 2% for particulate masses, 5-10% for abundant species (SO<sub>4</sub><sup>2-</sup>,  $NO_3^{-1}$ , major crustal elements in the coarse fraction and SO42, NH4+, K+, BC in the fine fraction) and 10-20% for other species. BC was measured only for fine samples. For NO<sub>3</sub>, only values for the coarse fraction were considered as many values for the fine fraction were below the detection limit.

# 4. Comparison of chemical compositions of PM<sub>10</sub> at the urban and rural sites

The mean concentrations of aerosol constituents at the two sites and the urban-torural ratios (URR) are shown in Table 1 and Figure 2, respectively. For the fine fraction, the concentrations of fine particulate mass (FM) and most of components are almost similar at the two sites. Meanwhile, coarse particulate mass (CM) and coarse mineral components are from 1.2 to 2 times more abundant in Hanoi. The URRs are highest (2.1 - 4.6) for Zn, Pb, Ca and Ca<sup>2+</sup> in both coarse and fine fractions, reflecting the urban-rural contrast in traffic and construction activities. On the other hand, NH<sub>4</sub><sup>+</sup>, Na (Na<sup>+</sup>) and Cl (Cl<sup>-</sup>) are more abundant at the rural site.

As it can be expected, the concentrations of ionic species  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $CI^-$  are less than the corresponding values for Ca, Mg, K, Cl. The proportion for a chemical element (E) occurring in particulates as a soluble cation or anion (I) can be estimated using the regression relationship

$$[I] = a[E] + b$$
 (1)

where the square brackets refer to the concentration of the species inside. The regression coefficients a are rather similar for the two sites (Table 2). It is worthy noting the high proportions of alkaline cations Ca<sup>2+</sup> in both coarse and fine fractions (> 72%) and  $K^{+}$  in the fine fraction (> 90%). These values are much larger than those found in original rocks and soils (Park et al., 2001; Vietnam National Institute for Soil and Fertilizers, 2003) due to the intereaction of particulates with sulfur and nitrogen gases in the atmosphere leading to the formation of secondary sulphate and nitrate.



Figure 2. URR for coarse and fine PM<sub>10</sub> chemical components

Table 1 Mean concentrations of aerosol constituents (ng m<sup>-3</sup>) in Hanoi (urban) and Lucnam (rural)

|                              | Hanoi (urban) |       | Lucnam (rural) |       |
|------------------------------|---------------|-------|----------------|-------|
|                              | coarse        | fine  | coarse         | fine  |
| BC                           |               | 5321  |                | 4711  |
| Al                           | 1225          | 255   | 881            | 312   |
| Ca                           | 1958          | 330   | 710            | 150   |
| Ca <sup>2+</sup>             | 1735          | 264   | 541            | 126   |
| CI                           | 339           | 38    | 357            | 50    |
| CI-                          | 244           | 20    | 264            | 19    |
| Fe                           | 780           | 175   | 439            | 121   |
| K                            | 481           | 563   | 395            | 570   |
| $K^+$                        | 216           | 546   | 132            | 583   |
| Mg                           | 488           | 157   | 424            | 195   |
| Mg <sup>2+</sup>             | 95            | 34    | 62             | 24    |
| Mn                           | 25            | 21    | 13             | 15    |
| Na⁺                          | 209           | 115   | 236            | 133   |
| ${\sf NH_4}^+$               | 152           | 1237  | 204            | 1556  |
| NO <sub>3</sub> <sup>-</sup> | 233           |       | 150            |       |
| Pb                           | 30            | 111   | 11             | 45    |
| Si                           | 2569          | 559   | 2076           | 646   |
| $SO_4^{2^-}$                 | 2537          | 6022  | 1614           | 6763  |
| Ti                           | 75            | 12    | 51             | 12    |
| V                            | 4             | 3     | 4              | 3     |
| Zn                           | 82            | 133   | 18             | 43    |
| CM                           | 36411         |       | 19071          |       |
| FM                           |               | 31063 |                | 32141 |
|                              |               |       |                |       |

#### 5. PMF Receptor modeling

#### 5.1. Methodology

Positive Matrix Factorization (PMF) developed by Paatero and Tapper (1994) was applied for source receptor modeling. In this work, the procedure for estimating the errors of data points and selecting PMF working parameters was similar to that used previously (Hien et al., 2004). The appropriate factor model was achieved by varying the number of extracted factors and other working parameters and looking for a stable and physically interpretable factor model.

#### Table 2

Regression coefficient a (± standard error) in the regression relationship between ionic (I) and elemental (E) concentrations [I] = a[E] + b. The values of *b* are insignificant and not shown

|                       | Hanoi         |               | Lucnam  |                  |
|-----------------------|---------------|---------------|---|------------------|
|                       | coarse        | fine          | coarse  | fine             |
| Ca <sup>2+</sup> - Ca | $0.86\pm0.05$ | $0.79\pm0.03$ | $0.72\ \pm 0.02$  | $0.77\ \pm 0.03$ |
| Cl <sup>-</sup> - Cl  | $0.78\pm0.02$ | $0.34\pm0.06$ | $0.72\ \pm 0.03$  | $0.19\ \pm 0.04$ |
| K <sup>+</sup> - K    | $0.49\pm0.04$ | $0.90\pm0.03$ | $0.42\ \pm 0.02$  | $0.98\pm0.02$    |
| Mg <sup>2+</sup> - Mg | $0.07\pm0.02$ | $0.07\pm0.02$ | $0.07 \hspace{0.1 cm} \pm \hspace{0.1 cm} 0.02 \hspace{0.1 cm}$ | $0.07 \pm 0.02$  |
|                       |               |               |   |                  |

#### 5.2. Sources of coarse PM<sub>10</sub>

The six source factors resolved by PMF for the rural site were also found for the urban site. The similarity between the composition profiles for the two sites can be seen in Fig. 3. The [Ca]/[Si] ratio, which can be used for characterizing the alkalinity of MD particles, consistently decreases from factor 1 to 4. Carich particles in factors 1-2 are likely originated from the soil, while Ca-depleted particles in factors 3-4 probably indicate coal fly ash. This is supported by the results of source apportionment (Figs. 5-6). The abundances of MD particles in factors 1-2 are much higher in

Hanoi than in Lucnam reflecting the urbanrural contrast in traffic and construction/road works.



Figure 3. Source composition profiles of coarse PM<sub>10</sub>



Figure 4. Source composition profiles of fine PM<sub>10</sub>

Factor 1 represents Ca-richest MD particles ([Ca]/[Si] > 1) at both sites. This factor is called soil-nitrate, as about 90% of the measured  $NO_3^{-1}$  mass is incorporated into these particles.

Besides nitrate, sulphate is also bound to Carichest MD particles in factor 1, but a larger amount of sulphate appears in factor 2, which does not contain nitrate. Factor 2 can be called soil-sulphate.

Coarse mode sulphate also appears in factor 3, and is insignificant in factor 4 (Fig. 3). Because sufficient time is required for sulphate to be built up on MD particles, factors 3 seems to represent coal fly ash from distant sources, while factor 4 indicates local coal burning sources. There are major coal burning sources in the Red River delta, which can affect both sites, such as power, cement and chemical plants.

NH<sub>4</sub><sup>+</sup> is not bound to mineral particles in factors 1-4. It appears in association with SO<sub>4</sub><sup>2-</sup> in factor 5, which is the largest source of sulphate and ammonium at both sites. This factor is called coarse ammonium sulphate (CAS), which is formed from locally emitted precursor gases, unlike fine ammonium sulphate, which is a major component of LRT aerosols (Hien et al., 2004). Factor 5 contains little mineral particles (Fig. 3), suggesting that ammonium sulphate is bound to the organic fraction of soil dust. The high enrichment of K and Zn in these particles seems to support this suggestion, as K and Zn are abundant in plant tissues.



Figure 5. Source apportionment of coarse PM<sub>10</sub> in Hanoi

Factor 6 with high loadings of Cl, Cl<sup>-</sup> and Na<sup>+</sup> obviously indicates marine aerosols. This factor has maximum impact in February-April in association with southeasterly flows from the Gulf of Tonkin to the Red River delta. As a result, a high correlation (r = 0.84) was found between the marine aerosol G-factors for the two sites.





The above factors could explain more than 90% of the mean concentrations of most species measured at both sites. For Pb and Zn, however, the 6-factor model could explain only 50 - 60% of the mean concentrations measured in Hanoi. These elements emerge only on the 7-th factor, which can be related to vehicle emissions. Lead and zinc particles from vehicle emissions occur mainly in the sub-micron size range. These fine particles may then be attached to the coarse road dust particles, so that Pb and Zn are found to coexist with mineral species in factor 7. The significant anticorrelation (r = -0.43) between relative humidity and the G-factor 7 fully supports its assignment to road dust. The results of source apportionment are shown in Figs.5-6.

#### 5.3. Sources of fine PM<sub>10</sub>

Five sources already discussed above were also found for fine PM<sub>10</sub> at both sites, namely marine aerosol, distant and local coal burning sources, traffic and soil dust (Fig. 4). The high coarse-fine pair correlations of G-factors indicate their common origins. Two other sources resolved only for the fine fraction are LRT aerosol containing fine ammonium sulphate and biomass burning. The impacts of LRT aerosol are similar at the two sites (36%), as it can be expected. Meanwhile, biomass burning is about two times stronger at the rural site.







## Figure 8. Source apportionment of fine PM<sub>10</sub> in Lucnam

Thus, six sources of fine PM<sub>10</sub> were found to be similar at the two sites, namely LRT, distant and local coal burning, soil dust, CI-depleted marine aerosol and biomass burning. The similarities of their composition profiles are shown in Figure 4. The seventh source is traffic for Hanoi and fine ammonium sulphate for Lucnam. Unlike LRT aerosol, fine ammonium sulphate is formed from local sources of precursor gases. The results of source apportionment are shown in Figs. 7-8.

#### 6. Conclusion

While CM is about two times higher in Hanoi than in Lucnam (37.8  $\mu$ g m<sup>-3</sup> vs. 19.1  $\mu$ g m<sup>-3</sup>), FM is almost similar at the two sites (31  $\mu$ g m<sup>-3</sup>). This finding was justified by the results of PMF receptor modeling. The difference in CM reflects the urban-rural contrast in traffic and construction/road works, the main producers of soil dust particles. The insignificant difference in FM is due to the similar impacts at the two sites of LRT aerosol (36%) and fine coal fly ash (30 -37%). Furthermore, the contribution from vehicle emissions in Hanoi is balanced by the stronger biomass burning emission in Lucnam. Coal fly ash is about 1.3 times more abundant in Lucnam.

Coarse nitrate is 1.5 times more abundant in Hanoi than in Lucnam, reflecting the urban-rural contrast in traffic. Conversely, ammonium is more abundant (30%) at the rural site. Concerning sulphate, the urban-rural difference is insignificant, confirming the rather similar impact of coal burning at the two sites.

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