Seasonal variation of PAH and molecular markers for biomass burning in fine particulate mountain aerosol at Jeju, Korea

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Biomass burning is an important primary source of soot and organic particulate matter which scatters and absorbs incident solar radiation, thereby affecting the earth’s albedo as well as decreasing visibility. East Asian nations are undergoing the most rapid industrialization in the world, of which downwind, the North Pacific region, is anticipated to be impacted by increasing air pollutants, particularly from pyrogenic sources (e.g., biomass burning, motorvehicles, and industrial and residential emissions). The monitoring at the Jeju Island, Korea, demonstrated that both carbon species seasonal trends with considerable elevation in winter to spring seasons and minor maxima in mid-summer. However, it was not clear whether the observed fluctuations in the atmospheric carbon species are stem from a single combustion source. The study aimed to investigate seasonal variations of polycyclic aromatic hydrocarbons (PAHs) molecular markers for biomass burning in fine particulate mountain aerosols at Mt. Halla, Jeju-do, and to elucidate predominant sources of combustions.

Materials and Methods
On the declive of Mt. Halla, Jeju Island, Korea (33.36N, 126.47E, 1100 m a.s.l.), located about 100 km south of the toe of Korean Peninsula, fine aerosols (PM2.5) were collected on quartz fiber filters, normally with the time resolution of 10-15 days. The samplers were operated at a flow rate between 16.5 and 24.5 L min$^{-1}$ and normally more than 400 m$^3$ of air was drawn through quartz fiber filters which were pre-combusted at 850C to minimize their organic contamination.

A portion of each filter was spiked with a mixture of deuterated surrogates, and then extracted under mild sonication three times with dichloromethane/methanol (95:5 v/v), followed by three successive methanol extractions. An aliquot of the extract was analyzed for levogulcosan (LG), and resin diterpenoids after TMS-derivertization with BSTFA by using capillary-GC/MS (SIM). The rest of the extract was purified through DMF cleanup procedure and 10% deactivated SiO$_2$ column chromatography according to the method described elsewhere$^1$ and then analyzed for PAHs by using a capillary-GC/MS (SIM).

Results and Discussion
1) Sum of 3-6 rings parental PAH concentrations ranging 0.05 to 7 ng m$^3$ showed seasonal variation similar to BC. That is, Total-PAHs become highest in winter-spring period and a small, but distinctive maximum was found in mid-summer.

2) PAHs observed at the study site were mostly combustion origin and showed intense signal in winter and several minor maxima in summer, which may reconfirm our preliminary observation of optical-BC at the same site.

3) Observations of LG and resin diterpenoid markers evidenced biomass (or vegetative materials) to be a significant source of combustion to the study site.

4) Combination of PAHs source diagnostic isomer pair ratios and biomass burning tracers revealed that biomass burning (or vegetative fuel combustion) contributions intermittently overwhelmed that from fossil fuel combustion.

5) The intense signals of LG/PAHs ratio in summer were characterized by airmass from East-China sea coastal area to South East Asia region, while those in fall and in winter seemed to be influenced more strongly by airmass from inland areas. On the other hand, Pinaceae combustion signals were characterized by airmass from Korea-Western Japan and its vicinity.

6) Intense PAHs signal with overwhelming contribution by biomass burning under westerly dominating condition in winter may explain, at least, partly recently reported modern carbon $^{14}$C-signature of atmospheric PAHs in winter in Japan$^1$.

References