# Particle-bound polycyclic aromatic hydrocarbons (PAHs) in typical urban of Yunnan-Guizhou Plateau: characterization, sources and risk assessment


Yaoqian Zhong[a], Bingxin Xia[a], Jianwu Shi [1a], Ping Ning [2a], Chaoneng Zhang[a], Xinyu Han[a] and Jiming Hao[a,b]

[a]Kunming University of Science and Technology
[b]Tsinghua University

[1]Corresponding author at: Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, No.727, Jingming South Road, Chenggong District, Kunming, China. Tel.:+86 871 6592 0508. Email address: shijianwu2000@sina.com

[2]Corresponding author at: Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, No.727, Jingming South Road, Chenggong District, Kunming, China. Tel.:+86 871 6592 0508. Email address: ningping58@sina.com.cn

**Abstract**

Monthly particle-phase ambient samples collected at six sampling locations in Yuxi, a high-altitude city on the edge of Southeast Asia, were measured for particle-associated PAHs. As trace substances, polycyclic aromatic hydrocarbons (PAHs) are susceptible to the influences of meteorological conditions, emissions, and gas-particulate partitioning and it is challenging job to precise quantify the source and define the transmission path. The daily concentrations of total $PM_{2.5}$-bound PAHs ranged from 0.65 to 80.76 ng/m$^3$, with an annual mean of 11.94 ng/m$^3$. Here, we found that the concentration of $PM_{2.5}$-bound PAHs in winter was significantly higher than that in summer, which was mainly due to source and meteorology influence. The increase of fossil combustion and biomass burning in cold season became the main contributors of PAHs, while precipitation and low temperature exacerbated this difference. According to the concentration variation trend of $PM_{2.5}$-bound PAHs and their relationship with meteorological conditions, a new grouping of PAHs is applied, which suggested that PAHs have different environmental fates and migration paths. A combination of source analysis and trajectory model supported local sources from combustion of fossil fuel and vehicle exhaust contributed to the major portion on PAHs in particle, but on the Indochina Peninsula the large number of pollutants emitted by biomass burning during the fire season would affect the composition of PAHs through long-range transporting. Risk assessment in spatial and temporal variability suggested that citizens living in industrial areas were higher health risk caused by exposure the $PM_{2.5}$-bound PAHs than that in other regions, and the risk in winter was three times than in summer.

**Keywords: Particle-associated PAHs, Fine particle, Source appointment, Group analysis, Risk assessment, Biomass burning**

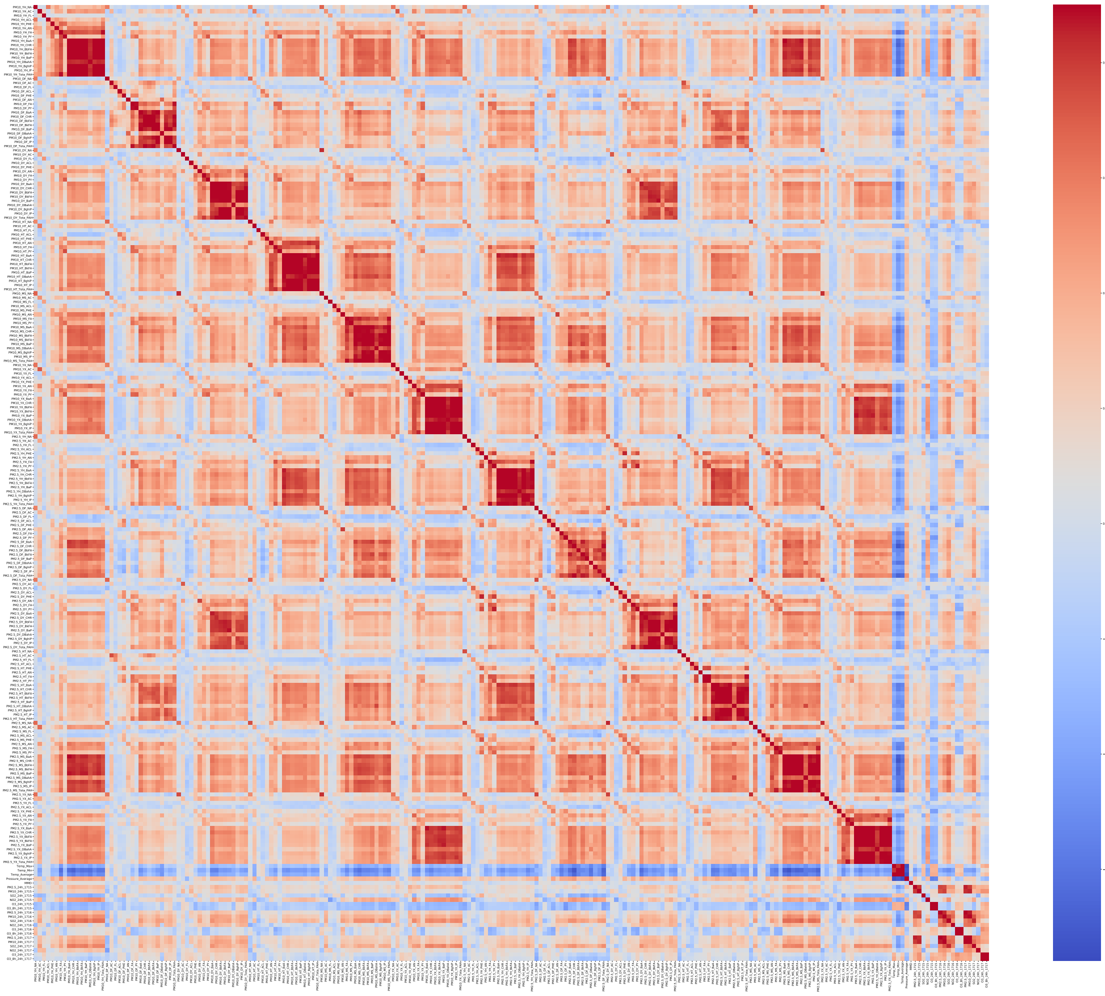

Figure A1: Heat map of PAH compounds in $PM_{2.5}$ with meterorology, pollutants, correlation coefficent calculated from daily PAH concentrations. Temp_Max: maximum ambient temperature of the day, Temp_Min: minmum ambient temperature of the day, Temp_Mean: average daily ambient temperature, Pressure_Mean: average daily ambient pressure, MMD: maximum mixed layer height of the day, PM2.5: average daily concentration of $PM_{2.5}$, PM10: average daily concentration of $PM_{10}$, SO2:average daily concentration of $SO_2$, NO2: average daily concentration of $NO_2$, O3: average daily concentration of $O_3$, O3(8h): maximum 8-hour moving average concentration of $O_3$, CO: average daily concentration of CO, Automatic environmental monitoring station ID: 1715, 1716, 1717.

Table A1: Comparison of average PAH concentrations in $PM_{2.5}$ and $PM_{2.5-10}$ with other cities ($ng/m^3$)

| PAHs | YH | DF | DY | HT | MS | YX | Mean* | Mean** | Tianjin[a] | Taiyuan[b] | Kunming[c] | Madrid[d] | Italy[e] | Malaysia[f] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| NA | 0.31 | 0.19 | 0.26 | 0.27 | 0.27 | 0.26 | 0.26 | 0.07 | 0.26 | 0.18 | 0.27 | 0.06 | N.A | 0.09 |
| AC | 0.31 | 0.35 | 0.37 | 0.25 | 0.25 | 0.25 | 0.30 | 0.01 | 0.3 | 0.24 | 0 | 0.003 | N.A | 0.12 |
| FL | 0.69 | 0.64 | 0.68 | 0.72 | 0.67 | 0.66 | 0.68 | −0.03 | 0.89 | 1.6 | 0.04 | 0.023 | 0.03 | 0.06 |
| ACL | 0.64 | 0.58 | 0.58 | 0.65 | 0.54 | 0.60 | 0.60 | 0.10 | 0.54 | 0.42 | 0.94 | N.A | N.A | 0.03 |
| PHE | 0.44 | 0.44 | 0.42 | 0.34 | 0.36 | 0.46 | 0.41 | 0.16 | 11.2 | 2.42 | 2.05 | 0.136 | 0.23 | 0.04 |
| AN | 0.04 | 0.07 | 0.05 | 0.03 | 0.02 | 0.03 | 0.04 | 0.05 | 8.19 | 3.02 | 0.18 | 0.008 | 0.13 | 0.04 |
| FA | 1.56 | 0.78 | 1.63 | 1.21 | 1.16 | 1.54 | 1.31 | 0.24 | 19.2 | 6.75 | 2.11 | 0.208 | 0.42 | 0.09 |
| PY | 1.18 | 0.72 | 1.32 | 1.04 | 0.87 | 1.14 | 1.04 | 0.14 | 16.5 | 4.91 | 3.1 | 0.261 | 0.49 | 0.07 |
| BaA | 0.74 | 0.51 | 0.79 | 0.49 | 0.56 | 0.85 | 0.66 | 0.14 | 11.2 | 12.7 | 1.91 | 0.041 | 0.47 | 0.04 |
| CHR | 1.09 | 0.70 | 1.19 | 0.74 | 0.85 | 1.12 | 0.95 | 0.20 | 9.41 | 17.9 | 3.38 | 0.098 | 0.5 | 0.09 |
| BbFA | 1.52 | 0.69 | 1.72 | 1.07 | 1.20 | 1.47 | 1.28 | 0.21 | 8.32 | 16.3 | 3.54 | 0.067 | 0.37 | 0.57 |
| BkFA | 0.65 | 0.56 | 0.83 | 0.45 | 0.51 | 0.68 | 0.62 | 0.07 | 4.46 | 10.4 | 1.65 | N.A | 0.32 | 0.25 |
| BaP | 1.02 | 0.64 | 1.39 | 0.73 | 0.83 | 1.10 | 0.95 | 0.14 | 7.43 | 13.8 | 3.02 | N.A | 0.21 | 0.3 |
| DBahA | 0.10 | 0.06 | 0.09 | 0.07 | 0.07 | 0.12 | 0.08 | 0.04 | 0.96 | 9.53 | 0.09 | N.A | 0.2 | 0.16 |
| BghiP | 1.54 | 0.89 | 2.20 | 1.20 | 1.30 | 1.52 | 1.44 | 0.18 | 6.17 | 10.1 | 3.08 | N.A | 0.12 | 0.54 |
| IP | 1.41 | 0.76 | 1.94 | 1.11 | 1.23 | 1.48 | 1.32 | 0.18 | 7.98 | 9.56 | 2.91 | N.A | 0.13 | 0.36 |
| $\sum$PAHs | 13.24 | 8.58 | 15.46 | 10.37 | 10.69 | 13.29 | 11.94 | 1.92 | 113.01 | 119.83 | 28.26 | 0.905 | 3.62 | 2.79 |

* PAH concentrations in $PM_{2.5}$
** PAH concentrations in $PM_{2.5-10}$
[a] Shi et al 2010.
[b] Li et al 2014.
[c] Bi et al 2015.
[d] Barrado et al 2012b.
[e] Martellini et al 2012.
[f] Khan et al 2015.

Table A2: Diagnose ratio of $PM_{2.5}$-bound PAHs.

| Source and season | IP/(IP+BghiP) | BaP/BghiP | FA/(FA+PY) | BaA/(BaA+CHR) | AN/(AN+PHE) |
|---|---|---|---|---|---|
| Liquid fossil fuel combustion | 0.2-0.5[a] | | 0.4-0.5[a] | | |
| Coal combustion | 0.56[b,c] | 0.9-6.6[c,d] | 0.57[c,e] | 0.46[c,e] | >0.1[i] |
| Coke combustion | 0.90[f] | 0.85[f] | 0.50[f] | 0.30[f] | |
| Wood combustion | 0.62[c] | | 0.51[c,g] | 0.43[c] | |
| Gasoline engine | 0.18[c] | 0.5-0.6[b] | <0.5[c] | 0.49[c] | <0.1[i] |
| Diesel engine | 0.35-0.7[c] | 0.3-0.4[h] | >0.5[c] | 0.68[c] | <0.1[i] |
| Iron smelter | 0.37[f] | 0.71[f] | 0.40[f] | 0.48[f] | |
| Spring | 0.48 | 0.57 | 0.31 | 0.32 | 0.02 |
| Summer | 0.46 | 0.45 | 0.56 | 0.35 | 0.03 |
| Autumn | 0.56 | 0.67 | 0.39 | 0.43 | 0.09 |
| Winter | 0.50 | 0.78 | 0.33 | 0.44 | 0.18 |

[a] Li et al 2006.
[b] Ravindra et al 2008.
[c] Kong et al 2010.
[d] Akyüz and Çabuk 2008.
[e] Galarneau 2008.
[f] Manoli et al 2004.
[g] Gschwend and Hites 1981.
[h] Barrado et al 2012a.
[i] Yunker et al 2002.

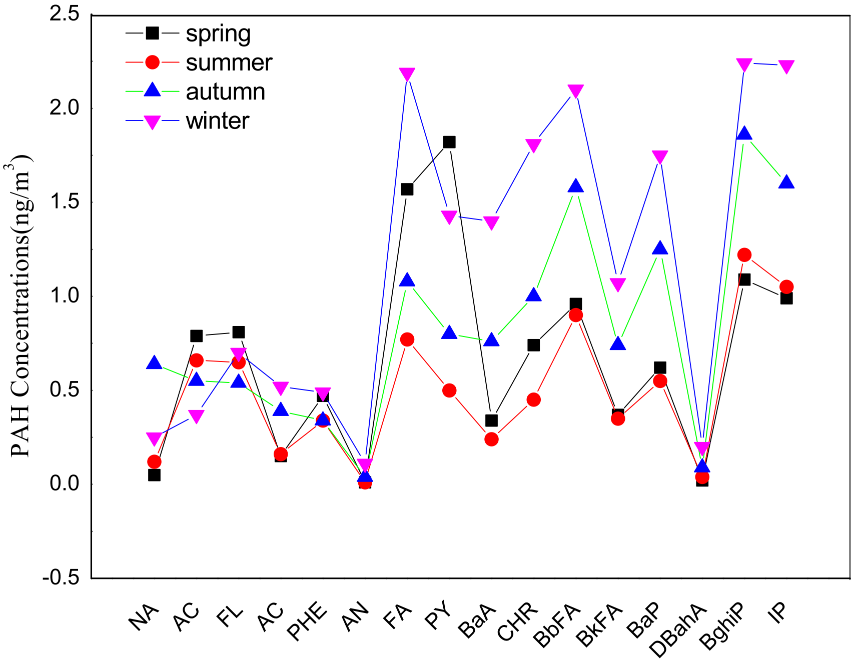


Figure A2: PAH compounds in $PM_{2.5}$ Seasonal distribution.

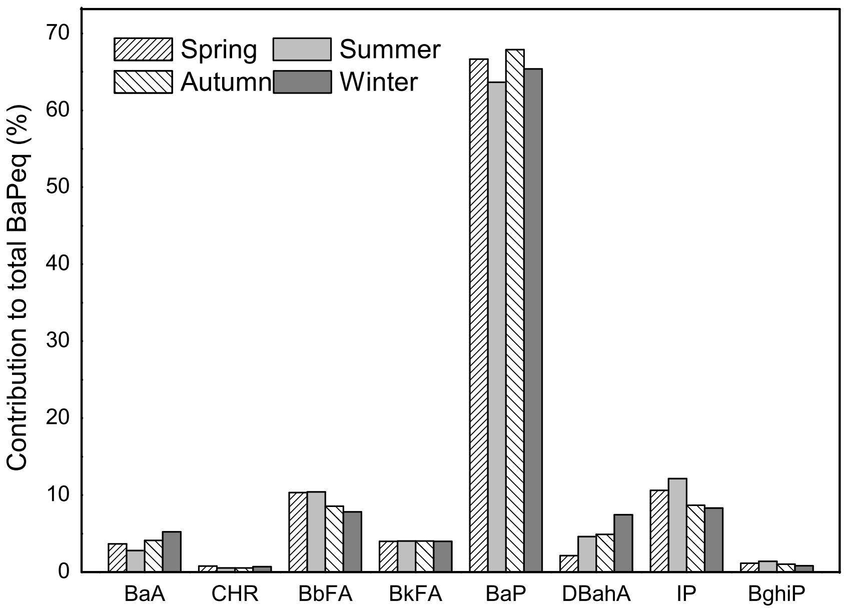


Figure A3: Relative contributions of individual PAHs in fine particulate seasonal distribution.

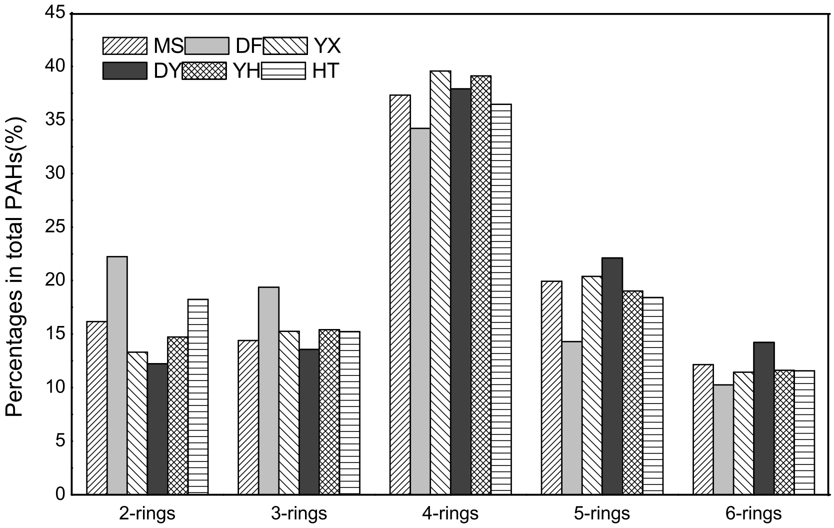


Figure A4: Spatial distribution of various PAHs in $PM_{2.5}$ grouped by ring size.

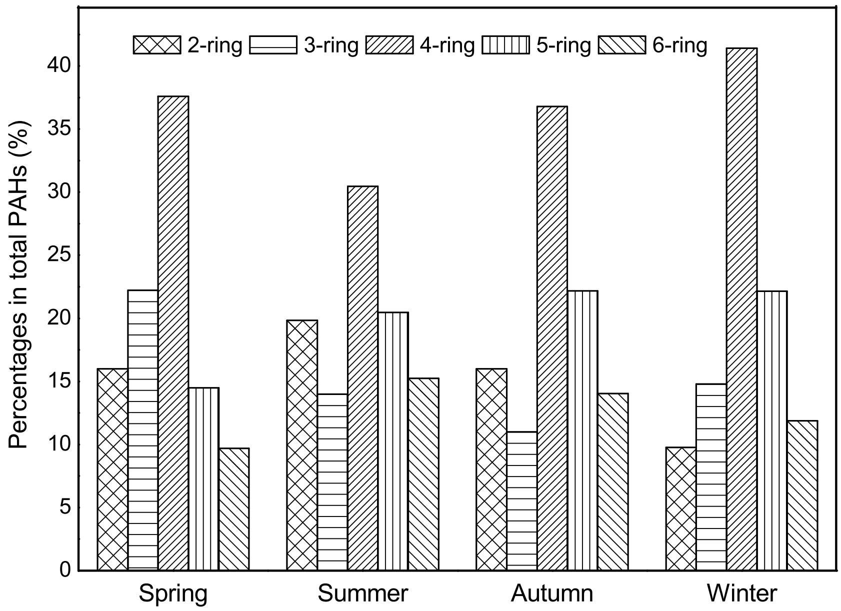


Figure A5: Seasonal distribution of PAHs in $PM_{2.5}$ grouped by ring size.

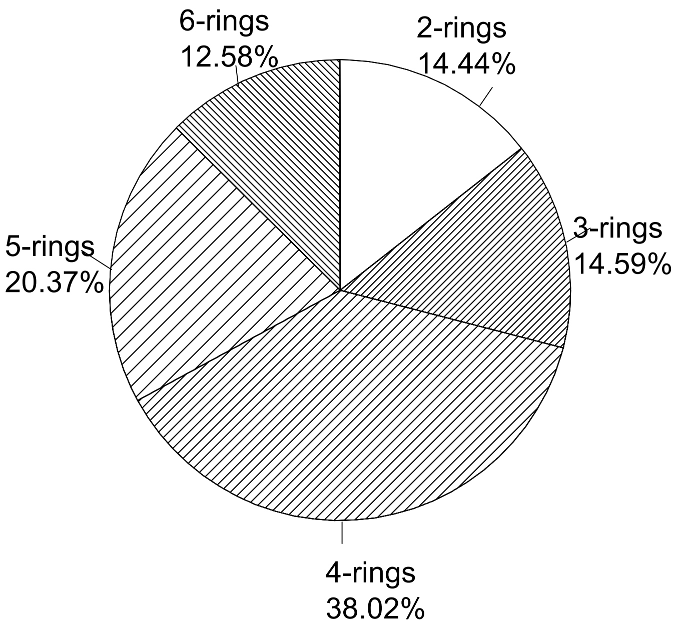


Figure A6: $\sum$PAHs mass ratio by ring size.

# Bibliography


Akyüz M, Çabuk H (2008). Particle-associated polycyclic aromatic hydrocarbons in the atmospheric environment of zonguldak, turkey. Science of the Total Environment, 405(1-3):62–70

Barrado AI, Garcia S, Barrado E, Perez RM (2012a). $\mathbf{PM}_{2.5}$-bound pahs and hydroxy-pahs in atmospheric aerosol samples: correlations with season and with physical and chemical factors. Atmospheric Environment, 49(3):224–232

Barrado AI, Garcia S, Barrado E, Perez RM (2012b). $Pm_{2.5}$-bound pahs and hydroxy-pahs in atmospheric aerosol samples: correlations with season and with physical and chemical factors. Atmospheric Environment, 49(3):224–232

Bi L, Hao J, Ning P, Shi J, Shi Z, Xu X (2015). Characteristics and sources apportionment of $pm_($2.5)-bound pahs in kunming. China Environmental Science, 35(3):659–667

Galarneau E (2008). Source specificity and atmospheric processing of airborne pahs: implications for source apportionment. Atmospheric Environment, 42(35):8139–8149

Gschwend PM, Hites RA (1981). Fluxes of polycyclic aromatic hydrocarbons to marine and lacustrine sediments in the northeastern united states. Geochimica Et Cosmochimica Acta, 45(12):2359–2367

Khan MF, Latif MT, Lim CH, Amil N, Jaafar SA, Dominick D, et al (2015). Seasonal effect and source apportionment of polycyclic aromatic hydrocarbons in $pm_{2.5}$. Atmospheric Environment, 106(178):178–190

Kong S, Ding X, Bai Z, Han B, Chen L, Shi J, Li Z (2010). A seasonal study of polycyclic aromatic hydrocarbons in $\mathbf{PM}_{2.5}$ and $\mathbf{PM}_{2.5-10}$ in five typical cities of liaoning province, china. Journal of Hazardous Materials, 183:70–80

Li J, Zhang G, Li XD, Qi GQ S Hand Liu, Peng XZ (2006). Source seasonality of polycyclic aromatic hydrocarbons (pahs) in a subtropical city, guangzhou, south china. Science of the Total Environment, 355(1-3):145–155

Li RJ, Kou XJ, Geng H, Dong C, Cai ZW (2014). Pollution characteristics of ambient $pm_{2.5}$-bound pahs and npahs in a typical winter time period in taiyuan. Chinese Chemical Letters, 25(5):663–666

Manoli E, Kouras A, Samara C (2004). Profile analysis of ambient and source emitted particle-bound polycyclic aromatic hydrocarbons from three sites in northern greece. Chemosphere, 56(9):867–878

Martellini T, Giannoni M, Lepri L, Katsoyiannis A, Cincinelli A (2012). One year intensive $pm_{2.5}$ bound polycyclic aromatic hydrocarbons monitoring in the area of tuscany, italy. concentrations, source understanding and implications. Environmental Pollution, 164(1):252–258

Ravindra K, Sokhi R, Grieken RV (2008). Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmospheric Environment, 42(13):2895–2921

Shi J, Peng Y, Li W, Qiu W, Bai Z, Kong S, et al (2010). Characterization and source identification of $pm_{10}$-bound polycyclic aromatic hydrocarbons in urban air of tianjin, china. Aerosol & Air Quality Research, 10(5):507–518

Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002). Pahs in the fraser river basin: a critical appraisal of pah ratios as indicators of pah source and composition. Organic Geochemistry, 33(4):489–515