

THE EFFECTIVENESS OF GEOCHEMICAL PARAMETERS FOR POLYCYCLIC AROMATIC HYDROCARBONS SOURCE APPORTIONMENT IN TOPSOIL

Z. H. Zhang^{*1,2}, Y. Liu^{1,2}, L. Zeng^{1,2}, J. J. Fei^{1,2}, T.T. Wan^{1,2}

¹. China University of Petroleum, Beijing, China;

². State Key Laboratory of Petroleum Resources and Prospecting, Beijing, China

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous persistent organic pollutants (POPs) in the environment, which may exert adverse influence on soil environment quality. Due to extremely complicated and diverse emission sources of PAHs, it is indispensable to establish an effective methodology for their source apportionment. To achieve this research purpose, the molecular marker parameters-based source apportionment for PAHs in soils is of great significance. These parameters are extensively used to identify the source of PAHs in air (Lee et al., 1982; Hwang et al., 2003; Zhang et al., 2005; Park et al., 2011; Tobiszewski et al., 2012); however, they have been explored in soil and sediment recently (Yunker et al., 2002; Yan et al., 2004; Huang et al., 2012). Once released into soils, chemical composition of PAHs may change. This could bring some uncertainty for their source identification in soils. Therefore, some researchers have doubted on the parameters used for pollution source apportionment of PAHs in soil (Zuo et al., 2007; Galarnau, 2008; Ravindra et al., 2008; Katsoyiannis et al., 2007; Dvorská et al., 2011; Huang et al., 2012). Vertical migration and microbial biodegradation may be responsible for the alteration of molecular marker composition of PAHs. Up to date, how the vertical migration and biodegradation influence on the molecular marker parameters remains unclear.

Objectives and Results

To better understand the influence of vertical migration and microbial degradation on the effectiveness of molecular biomarker parameters for PAHs source apportionment, it was proposed to analyze the fractionation effect of different PAH species during vertical migration process in the soil profiles based on the soil-column leaching simulation experiment, and compare the difference in anti-microbial degradation among different PAHs monomers based on the microbial degradation simulation experiment. The influence of vertical migration and microbial degradation on the effectiveness of molecular biomarker parameters for PAHs source apportionment in soil were preliminarily discussed.

The results of leaching simulation experiment indicate that: (1) The contents of both total and individual PAHs in topsoil are sharply decreased after leaching experiment, which indicate that the migration of PAHs has happened during the simulating experiments at different levels. The PAHs with low molecular weight (2-3 rings) are more readily to migrate to the deep horizon of the soil profile than the PAHs with high molecular weight (4-6 rings), implying that migration ability of different molecular weight PAHs are different obviously; (2) The migration rate of PAHs with different structure are various, for example, Ph > An, BaA > Chr, Fl > Py, I[1,2,3-cd]P > B[g,h,i]Pe; (3) The values of An/(An+Ph), BaA/(BaA+Chr), Fl/(Fl+Py), I[1,2,3-cd]P, B[g,h,i]Pe, C0/(C0+C1) and LMW/HMW in topsoil changed in different degrees after leaching experiment; (4) The leaching flow of water, TOC in soil and physicochemical property of PAHs have important influences on the migration of PAHs in soil column.

The results of simulation experiment for microbial degradation suggest that: (1) The degradation rate of different PAH monomers is significantly varying. After degraded for 28 days, the maximal degradation rate of phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene and chrysene is 25.3%, 35.6%, 20.1%, 19.2%, 9.7%, 10.2% and 20.0%, 9.0%, 15.0%, 13.0%, 4.0%, 6.0% in single and combined medium condition, respectively. In crude oil medium, the degradation efficiency of PAHs is more sophisticated. The degradation rate of low and middle molecular weight PAHs decreased with time. This may be due to the degradation of alkyl or high molecular weight PAHs to low molecular weight ones.

(2) Comparing the parameters before and after the degradation, Ant/(Ant+Phe), Fl/(Fl+Py), BaA/(BaA+Chr) and LMW/HMW have changed.

Conclusions

Some PAHs molecular marker parameters for source apportionment were changing during the leaching procedure. Thus, the effectiveness of these parameters should be reconsidered. In this research, Fl/(Fl+Py), An/(An+Ph) and LMW/HMW have changed sharply, whereas, BaA/(BaA+Chr) and IP/(IP+B[g, h, i]Pe) are relatively stable.

Microbial degradation can also influence on the effectiveness of some molecular marker parameters, such as Ant/(Ant+Phe), BaA/(BaA+Chr) and LMW/HMW, for PAHs source apportionment.

Acknowledgments: The research is supported by the National Natural Science Foundation of China (Grant No. 41373126).

References

- Galarneau, E., 2008. Source specificity and atmospheric processing of airborne PAHs: implications for source apportionment. *Atmospheric Environment* 42(35), 8139-8149.
- Huang, W., Wang, Z., Yan, W., 2012. Distribution and sources of polycyclic aromatic hydrocarbons (PAHs) in sediments from Zhanjiang Bay and Leizhou Bay, South China. *Marine pollution bulletin* 64(9), 1962-1969.
- Hwang, H. M., Wade, T. L., Sericano, J. L., 2003. Concentrations and source characterization of polycyclic aromatic hydrocarbons in pine needles from Korea, Mexico and United States. *Atmospheric Environment* 37(16), 2259-2267.
- Katsoyiannis, A., Terzi, E., Cai, Q. Y., 2007. On the use of PAH molecular diagnostic ratios in sewage sludge for the understanding of the PAH sources. Is this use appropriate? *Chemosphere* 69(8), 1337-1339.
- Lee, M. L., Vassilaros, D. L., Later, D., 1982. Capillary column gas chromatography of environmental polycyclic aromatic compounds. *International journal of environmental analytical chemistry* 11(3-4): 251-262.
- Park, S. U., Kim, J. G., Jeong, M. J., Songet, B.J., 2011. Source identification of atmospheric polycyclic aromatic hydrocarbons in industrial complex using diagnostic ratios and multivariate factor analysis. *Archives of environmental contamination and toxicology* 60(4), 576-589.
- Tobiszewski, M., Namieśnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. *Environmental Pollution*, 162, 110-119.
- Yan, B., Benedict, L., Chaky, D.A., Bopp, R.F., Abrajano, T.A., 2004. Levels and patterns of PAH distribution in sediments of the New York/New Jersey harbor complex. *Northeastern Geology and Environmental Sciences* 26(1/2), 113-122.
- Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R.H., 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.
- Zhang, X. L., Tao, S., Liu, W. X., Yang, Y., Zuo, Q., Liu S. Z., 2005. Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: a multimedia approach. *Environmental science & technology* 39(23), 9109-9114.
- Zuo, Q., Duan, Y. H., Yang, Y., Wang, X. J., Tao, S., 2007. Source apportionment of polycyclic aromatic hydrocarbons in surface soil in Tianjin, China. *Environmental Pollution* 147(2), 303-310.