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Historical record of effects of human activities on absolute and relative concentrations of Polycyclic aromatic hydrocarbons (PAHs) in Lake Chao, China

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Polycyclic aromatic hydrocarbons (PAHs) are attracting concern because of their potential toxicity, posing serious threats to health of humans and ecosystems (Kim et al., 2013; Zhao et al., 2016). Generally, similar to other contaminants' behaviors (Wu et al., 2001; Zhang et al., 2007, 2008; Lu et al., 2009), PAHs result from natural organic matter and activities of humans, the latter's contribution usually outweighing the inputs from other sources (Fernández et al., 2000; Srogi, 2007). So far, more than 200 PAHs have been discovered, and among them 16 PAHs were classified as priority pollutants by the US Environmental Protection Agency (Xia et al., 2012; Sun et al., 2016). Most PAHs are hydrophobic and either non-biodegradable or transformed to hydroxides that are slowly degraded. Due to their complex sources, PAHs have become ubiquitous in the environment (Kannan et al., 2005; Guo et al., 2011b; Nie et al., 2014; Ohura et al., 2015). Another reason for the persistence of PAHs is particularly due to their strong affinity to particulate matter. PAHs are only slowly degraded in anoxic phases of soils or sediments (Li et al., 2015) that are protected from solar insulation (Lorgeoux et al., 2016). When introduced into sediments, PAHs can be absorbed to suspended particles and transported into lakebed or seabed sediment, from which they can be re-released into the water or accumulated into organisms (Stout and Emsbo-Mattingly, 2008; Harris et al., 2011). Sediments serve as both a "sink" and potential "source" of PAHs such that contamination of sediments by PAHs is considered to be a critical problem in aquatic environments (Li et al., 2014). Occurrences of PAHs in aquatic sediments can be from depositions from the atmosphere, municipal runoff or oil spills (Li et al., 2014; Ohura et al., 2015). Monitoring of PAHs in sediment is useful because it not only provides insight about their fates in aquatic ecosystems, but can be used in assessments of risks to humans or wildlife or be used in forensic analyses to determine sources and monitor for status and trends of concentrations (Chen et al., 2013; Rahmanpoor et al., 2014; Floehr et al., 2015). In particular, PAHs are useful as markers of anthropogenic activities (Ravindra et al., 2008; Kim et al., 2013; Lee et al., 2015).

Some studies have quantitatively monitored PAHs in sediments to examine distributions, as well as sources, especially in some coastal waters or catchments surrounded by economically developed areas where greater concentrations of PAH were frequently detected (Karacık et al., 2009; Sun et al., 2016). Quantification of PAHs in cores of sediments can be used to assess historical loadings (Lorgeoux et al., 2016) and detailed information on a temporal scale (Tao et al., 2012). In China, cores of sediments from urban lakes, such as Tai

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Lake, Baiyangdian Lake, Dahuofang Reservoir, Dianchi Lake, Erhai Lake and even remote western lakes have been conducted by Guo et al. (2011a, 2011b), Lin et al. (2012), and Guo et al. (2013). Results of these studies indicated that reconstruction of histories of pollution with PAHs by investigating lacustrine core samples of sediments is helpful to understand pollution mechanisms and anthropogenic activities.

Lake Chao (Ch: *Chaohu*), located in Eastern China, is the only local source of water for millions of local residents in Anhui province. According to previous studies of contamination in this catchment, Lake Chao was found to be seriously polluted by eutrophication and heavy metal contamination, indicating an intense involvement of anthropogenic activities (Zan et al., 2011; Huo et al., 2013). However, little information was available on historical contamination in this area (Zan et al., 2011, 2012) and little information was available on concentrations of PAHs from anthropogenic activities. In order to understand and assess impacts of drastically increased anthropogenic activities on the aquatic ecosystem of Lake Chao, initial efforts were urgently needed to assess risks and determine current status and trends for sediments so that efficacy of control measures could be assessed.

Addressing the lack of information on deposition of PAHs due to human activities, a recent paper by Li et al. (2016) makes an effort to fulfill this objective by measuring concentrations of PAHs in sediments collected from Lake Chao. They collected sediment cores from Lake Chao and using the dated sediment cores (Fig. 1) reconstructed the history of contamination by matching concentrations of PAHs, corrected for focusing factors in each layer with dates assigned to each layer. Similar with most of the current sediment core record (Guo et al., 2011b), variation in total concentrations of PAHs, over time, was consistent with historical economic and social development, with three stages of loadings of PAHs, including a lag period in early socio-economic development, a period of innovation and development during the late 20th century, followed by a period during which standards and technologies were introduced to protect the environment. Because absolute and relative concentrations of PAH in sediments were influenced by sources, as well as sedimentological conditions (Li et al., 2016). Deposition fluxes and mass inventories of PAHs as a function of sedimentation in Lake Chao were reported (Fernández et al., 1999). Those authors calculated rates of deposition fluxes during each stage of economic development and remediation and restoration to determine how loadings of PAH to Lake Chao varied. A study by Azoury et al. (2013) demonstrated that depositional fluxes can be used to calculate a gradient for changes in rates of depositional flux. However, significant discrepancies were observed when predicted fluxes were compared to measured fluxes. In the innovation and development period, the rate of increase in integrated flux were almost 2–8 fold greater compared to that in the development lag period, which is consistent with intense anthropogenic activities that affected generation and emissions of PAHs in the catchment of Lake Chao at that time.

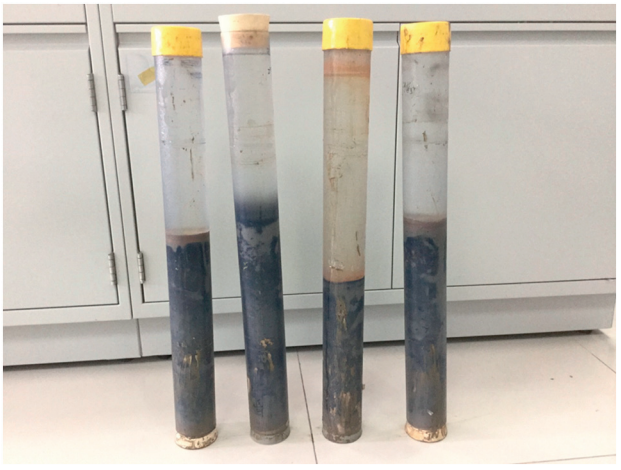

Fig. 1 – An example of sediment core samples collected from Lake Chao, Anhui, China. Photo courtesy of Professor Shouliang Huo, Institute of Water Environment Research, Chinese Research Academy of Environmental Sciences (CRAES), Beijing, China.

After the founding of the republic of China, the whole county underwent significant social and economic development, including Anhui province, where Lake Chao is situated. Generation of PAHs is affected by urbanization and industrialization. Local industrialization required additional energy, which was generated by combustion of coal and an increased utilization of petroleum hydrocarbons for the increased need for transport (Hafner et al., 2005; Wang et al., 2010). Usually, gross domestic product (GDP) and local population are the most effective indicators of urbanization and industrialization. To analyze socioeconomic influences, in the study by Li et al. (2016), PAHs were normalized to total organic carbon (TOC) when comparing with the population and GDP data. The strong positive correlation between normalized concentrations of PAH and the population and GDP, especially during the period of innovation and development demonstrated that loadings of PAHs to sediments of Lake Chao at that time were accompanied by the rapid growth and development of the social economy, urbanization and industrialization.

Besides effects of growth of the social economy on accumulation of PAHs in sediments, conditions of sedimentation during the period of interest act as an important influencing factor. It has been reported that grain size in lake sediment can be affected by changes in the hydrological situation (Molinaroli et al., 2009). Li's study (Li et al., 2016) did not ignore the implications of the record of deposition of PAHs in either the eastern or western locations. After 1963, when the Chao Dam was built, concentrations of PAHs in Lake Chao accelerated rapidly. Also, concentrations of PAHs in the western portion of the lake grow faster than that in the eastern portion of the lake. When comparing grain size, before and after construction of Chao Dam, it was interesting that finer grains simultaneously increased rapidly, and were significantly and positively correlated with total concentrations of PAHs attached to particles. These findings are consistent with conclusions of previous studies that changes in sedimentary conditions can also affect accumulation of PAHs in sediments of Lake Chao.

By investigating historical records of PAHs in cores of sediment from Lake Chao and evaluating factors influencing deposition of PAHs, scientists elucidated potential sources of PAHs and understanding of the effects of anthropogenic

activities in influencing loadings of PAHs. Overall, continued research contributing to evaluating the possibility of PAHs in sediments being secondary pollution and mechanisms of loading PAHs is needed in order to develop better measures to protect health of humans and the environment.

REFERENCES

Azoury, S., Tronczynski, J., Chiffoleau, J.F., Cossa, D., Nakhle, K., Schmidt, S., et al., 2013. Historical records of mercury, lead, and polycyclic aromatic hydrocarbons depositions in a dated sediment core from the Eastern Mediterranean. Environ. Sci. Technol. 47 (13), 7101–7109.

Chen, C.F., Chen, C.W., Dong, C.D., Kao, C.M., 2013. Assessment of toxicity of polycyclic aromatic hydrocarbons in sediments of Kaohsiung Harbor, Taiwan. Sci. Total Environ. 463–464, 1174–1181.

Fernández, P., Vilanova, R.M., Grimalt, J.O., 1999. Sediment fluxes of polycyclic aromatic hydrocarbons in European high altitude mountain lakes. Environ. Sci. Technol. 33 (21), 3716–3722.

Fernández, P., Vilanova, R.M., Martínez, C., Appleby, P., Grimalt, J.O., 2000. The historical record of atmospheric pyrolytic pollution over Europe registered in the sedimentary PAH from remote mountain lakes. Environ. Sci. Technol. 34 (10), 1906–1913.

Floehr, T., Scholz-Starke, B., Xiao, H., Koch, J., Wu, L., Hou, J., et al., 2015. Yangtze Three Gorges Reservoir, China: a holistic assessment of organic pollution, mutagenic effects of sediments and genotoxic impacts on fish. J. Environ. Sci. 38, 63–82.

Guo, J.Y., Liang, Z., Liao, H.Q., Tang, Z., Zhao, X.L., Wu, F.C., 2011a. Sedimentary record of polycyclic aromatic hydrocarbons in Lake Erhai, Southwest China. J. Environ. Sci. 23 (8), 1308–1315.

Guo, W., Pei, Y.S., Yang, Z.F., Chen, H., 2011b. Historical changes in polycyclic aromatic hydrocarbons (PAHs) input in Lake Baiyangdian related to regional socio-economic development. *J. Hazard. Mater.* 187 (1–3), 441–449.

Guo, J.Y., Wu, F.C., Liao, H.Q., Zhao, X.L., Li, W., Wang, J., Wang, L.F., Giesy, J.P., 2013. Sedimentary record of polycyclic aromatic hydrocarbons and DDTs in Dianchi Lake, an urban lake in Southwest China. *Environ. Sci. Pollut. Res.* 20 (8), 5471–5480.

Hafner, W.D., Carlson, D.L., Hites, R.A., 2005. Influence of local human population on atmospheric polycyclic aromatic hydrocarbon concentrations. Environ. Sci. Technol. 39 (19), 7374–7379.

Harris, K.A., Yunker, M.B., Dangerfield, N., Ross, P.S., 2011. Sediment-associated aliphatic and aromatic hydrocarbons in coastal British Columbia, Canada: concentrations, composition, and associated risks to protected sea otters. Environ. Pollut. 159 (10), 2665–2674.

Huo, S., Xi, B., Yu, X., Su, J., Zan, F., Zhao, G., 2013. Application of equilibrium partitioning approach to derive sediment quality criteria for heavy metals in a shallow eutrophic lake, Lake Chaohu, China. Environ. Earth Sci. 69 (7), 2275–2285.

Kannan, K., Johnson-Restrepo, B., Yohn, S.S., Giesy, J.P., Long, D.T., 2005. Spatial and temporal distribution of polycyclic aromatic hydrocarbons in sediments from Michigan inland lakes. Environ. Sci. Technol. 39 (13), 4700–4706.

Karacık, B., Okay, O.S., Henkelmann, B., Bernhöft, S., Schramm, K.W., 2009. Polycyclic aromatic hydrocarbons and effects on marine organisms in the Istanbul Strait. Environ. Int. 35 (3), 599–606.

Kim, K.-H., Jahan, S.A., Kabir, E., Brown, R.J.C., 2013. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. Environ. Int. 60, 71–80.

Lee, J.W., Won, E.-J., Raisuddin, S., Lee, J.-S., 2015. Significance of adverse outcome pathways in biomarker-based environmental risk assessment in aquatic organisms. J. Environ. Sci. 35, 115–127.

Li, G.L., Lang, Y.H., Gao, M.S., Yang, W., Peng, P., Wang, X.M., 2014. Carcinogenic and mutagenic potencies for different PAHs sources in coastal sediments of Shandong Peninsula. Mar. Pollut. Bull. 84 (1–2), 418–423.

Li, C.-H., Wong, Y.-S., Wang, H.-Y., Tam, N.F.-Y., 2015. Anaerobic biodegradation of PAHs in mangrove sediment with amendment of $NaHCO_3$. J. Environ. Sci. 30, 148–156.

Li, C., Huo, S., Yu, Z., Guo, W., Xi, B., He, Z., Zeng, X., Wu, F., 2016. Historical records of polycyclic aromatic hydrocarbon deposition in a shallow eutrophic lake: impacts of sources and sedimentological conditions. J. Environ. Sci. 41, 261–269.

Lin, T., Qin, Y.W., Zheng, B.H., Li, Y.Y., Zhang, L., Guo, Z.G., 2012. Sedimentary record of polycyclic aromatic hydrocarbons in a reservoir in Northeast China. *Environ. Pollut.* 163, 256–260.

Lorgeoux, C., Moilleron, R., Gasperi, J., Ayrault, S., Bonte, P., Lefevre, I., Tassin, B., 2016. Temporal trends of persistent organic pollutants in dated sediment cores: chemical fingerprinting of the anthropogenic impacts in the Seine River basin, Paris. Sci. Total Environ. 541, 1355–1363.

Lu, S.Y., Wu, F.C., Lu, Y.F., Xiang, C.S., Zhang, P.Y., Jin, C.X., 2009. Phosphorus removal from agricultural runoff by constructed wetland. Ecol. Eng. 35 (3), 402–409.

Molinaroli, E., Guerzoni, S., De Falco, G., Sarretta, A., Cucco, A., Como, S., et al., 2009. Relationships between hydrodynamic parameters and grain size in two contrasting transitional environments: the lagoons of Venice and Cabras, Italy. Sediment. Geol. 219 (1–4), 196–207.

Nie, J., Shi, J., Duan, X., Wang, B., Huang, N., Zhao, X., 2014. Health risk assessment of dietary exposure to polycyclic aromatic hydrocarbons in Taiyuan, China. J. Environ. Sci. 26 (2), 432–439.

Ohura, T., Sakakibara, H., Watanabe, I., Shim, W.J., Manage, P.M., Guruge, K.S., 2015. Spatial and vertical distributions of sedimentary halogenated polycyclic aromatic hydrocarbons in moderately polluted areas of Asia. Environ. Pollut. 196, 331–340.

Rahmanpoor, S., Ghafourian, H., Hashtroudi, S.M., Bastami, K.D., 2014. Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments of the Hormuz strait, Persian Gulf. Mar. Pollut. Bull. 78 (1–2), 224–229.

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

Srogi, K., 2007. Monitoring of environmental exposure to polycyclic aromatic hydrocarbons: a review. Environ. Chem. Lett. 5 (4), 169–195.

Stout, S.A., Emsbo-Mattingly, S.D., 2008. Concentration and character of PAHs and other hydrocarbons in coals of varying rank — implications for environmental studies of soils and sediments containing particulate coal. Org. Geochem. 39 (7), 801–819.

Sun, R.X., Lin, Q., Ke, C.L., Du, F.Y., Gu, Y.G., Cao, K., Luo, X.J., Mai, B.X., 2016. Polycyclic aromatic hydrocarbons in surface sediments and marine organisms from the Daya Bay, South China. Mar. Pollut. Bull. 103 (1–2), 325–332.

Tao, Y.Q., Xue, B., Yao, S.C., Deng, J.C., Gui, Z.F., 2012. Triolein embedded cellulose acetate membrane as a tool to evaluate sequestration of PAHs in lake sediment core at large temporal scale. Environ. Sci. Technol. 46 (7), 3851–3858.

Wang, X.P., Yang, H.D., Gong, P., Zhao, X., Wu, G.J., Turner, S., Yao, T.D., 2010. One century sedimentary records of polycyclic aromatic hydrocarbons, mercury and trace elements in the Qinghai Lake, Tibetan Plateau. Environ. Pollut. 158 (10), 3065–3070.

Wu, F.C., Qing, H.R., Wan, G.J., 2001. Regeneration of N, P, and Si near the sediment/water interface of lakes from southwestern China plateau. *Water Res.* 35 (5), 1334–1337.

Xia, K., Hagood, G., Childers, C., Atkins, J., Rogers, B., Ware, L., Armbrust, K., Jewell, J., Diaz, D., Gatian, N., Folmer, H., 2012. Polycyclic aromatic hydrocarbons (PAHs) in Mississippi seafood from areas affected by the Deepwater Horizon oil spill. Environ. Sci. Technol. 46 (10), 5310–5318.

Zan, F., Huo, S., Xi, B., Su, J., Li, X., Zhang, J., Yeager, K.M., 2011. A 100 year sedimentary record of heavy metal pollution in a shallow eutrophic lake, Lake Chaohu, China. J. Environ. Monit. 13 (10), 2788–2797.

Zan, F., Huo, S., Xi, B., Zhu, C., Liao, H., Zhang, J., Yeager, K.M., 2012. A 100-year sedimentary record of natural and anthropogenic impacts on a shallow eutrophic lake, Lake Chaohu, China. J. Environ. Monit. 14 (3), 804–816.

Zhang, M.Y., Wang, S.J., Wu, F.C., Yuan, X.H., Zhang, Y., 2007. Chemical compositions of wet precipitation and anthropogenic influences at a developing urban site in southeastern China. Atmos. Res. 84, 311–322.

Zhang, R.Y., Wu, F.C., Liu, C.Q., Fu, P.Q., Li, W., Wang, L.Y., Liao, H.Q., Guo, J.Y., 2008. Characteristics of organic phosphorus fractions in different trophic sediments of lakes from the middle and lower reaches of Yangtze River region and southwestern plateau, China. Environ. Pollut. 152, 366–372.

Zhao, M., Wang, W., Liu, Y., Dong, L., Jiao, L., Hu, L., Fan, D., 2016. Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments from the Bering Sea and western Arctic Ocean. Mar. Pollut. Bull. 104 (1–2), 379–385.