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Improved source apportionment of PAHs and Pb by integrating Pb stable isotopes and positive matrix factorization application (PAHs): A historical record case study from the northern South China Sea

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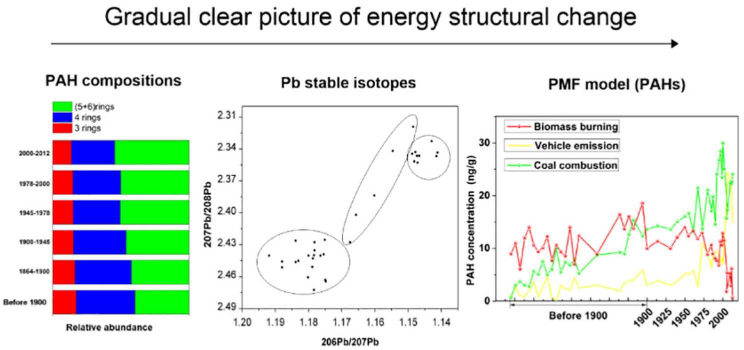
HIGHLIGHTS

- First-hand data of polycyclic aromatic hydrocarbons (PAHs) and lead (Pb) were investigated as a multi-indicator approach.
- The phasing-out of leaded gasoline in China was captured after the mid-1990s, while PAHs kept increasing in recent years.
- Integrated source apportionment methods were developed, providing a gradual clear picture of energy structural change.
- Biomass burning, coal combustion, and vehicle emissions accounted for 40± 20%, 41±13%, and 19±12% of PAHs through the core.
- It highlighted the growing importance of vehicle emissions since 2000.

GRAPHICAL ABSTRACT



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ABSTRACT

To obtain the historical changes of pyrogenic sources, integrated source apportionment methods, which include PAH compositions, diagnostic ratios (DRs), Pb isotopic ratios, and positive matrix factorization (PMF) model, were developed and applied in sediments of the northern South China Sea. These methods provided a gradually clear picture of energy structural change. Spatially, Σ_{15}PAH (11.3 to 95.5 ng/g) and Pb (10.2 to 74.6 μg/g) generally exhibited decreasing concentration gradient offshore; while the highest levels of PAHs and Pb were observed near the southern Taiwan Strait, which may be induced by accumulation of different fluvial input. Historical records of pollutants followed closely with the economic development of China, with fast growth of Σ_{15}PAH and Pb occurring since the 1980s and 1990s, respectively. The phasing-out of leaded gasoline in China was captured with a sharp decrease of Pb after the mid-1990s. PAHs and Pb correlated well with TOC and clay content for core sediments, which was not observed for surface sediments. There was an up-core increase of high molecular PAH proportions. Coal and biomass burning were then qualitatively identified as the major sources of PAHs with DRs.

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Positive matrix factorization (PMF)
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Furthermore, shift toward less radiogenic signatures of Pb isotopic ratios after 1900 revealed the start and growing importance of industrial sources. Finally, a greater separation and quantification of various input was achieved by a three-factor PMF model, which made it clear that biomass burning, coal combustion, and vehicle emissions accounted for 40 ± 20%, 41 ± 13%, and 19 ± 12% of PAHs through the core. Biomass and coal combustion acted as major sources before 2000, while contributions from vehicle emission soared thereafter. The integrated multi-methodologies here improved the source apportionment by reducing biases with a step-down and cross-validation perspective, which could be similarly applied to other aquatic systems.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and lead (Pb) are widespread and persistent contaminants mainly arise from anthropogenic activities, among which biomass burning, fossil fuel combustion, and waste incineration are the common predominant origins (Yunker et al., 1996; Azoury et al., 2013). Owning to their hydrophobic nature, both PAHs and Pb tend to associate with particulate matter and finally deposit to the sediments in aquatic systems (Harlavan et al., 2010; Parinos and Gogou, 2016; Gustafsson et al., 1997). In this context, sediment cores act as effective tool to reconstruct temporal trends of these combustion byproducts (Martins et al., 2010; Lima et al., 2003; Schneider et al., 2001). However, there are inevitable uncertainties for such construction due to the influence of some factors, including diagenesis and degradation processes, postdepositional transformations, and geochronological dating (Azoury et al., 2013; Louchouarn et al., 2012). The combination of PAHs and Pb could be used as a multi-indicator approach to possibly reduce such uncertainties, which have been successfully conducted in few studies (Leorri et al., 2014; Louchouarn et al., 2012; Vane et al., 2011).

Source apportionment of Pb and PAHs is always of great interest motivated by better environmental control and evidence in litigation. Discrimination of combustion sources can be afforded by diagnostic ratios (DRs) of PAHs (Yunker et al., 2002), which, however, involve just a portion of PAH data produced and provide only qualitative results. In addition, contribution of different sources may be obscured due to the intra-source variability and potential similarity in end-member signatures of PAHs (Galarneau, 2008; Tobiszewski and Namieśnik, 2012). Further, Pb stable isotopes, which are not obviously influenced by ordinary chemical, physical or biological fractionation processes (Gallon et al., 2005; Cheng and Hu, 2010), allows for better discrimination among different sources. Their merit is that each source has distinct or overlapping ranges (Komarek et al., 2008). For example, geogenic Pb is more radiogenic than Pb derived from an anthropogenic source (Komarek et al., 2008). However, the source apportionment using Pb stable isotopes can be quantified only in cases where all potential sources of Pb are characterized and have specific ratios, which are hardly to meet. To overcome the limitations of source apportionment mentioned above, additional tools need to be used for greater separation and further quantification of various inputs.

Positive matrix factorization (PMF), one of the receptor models based on the pollutant profiles observed, enables PAH source categories to be identified and quantified. It relies on several congeners rather than ratios between paired PAHs to describe individual sources (Liu et al., 2015), which renders them more persuasive and convincing. Moreover, it does not rely on prior knowledge of source information, and therefore is more practical. This method has been successfully applied in source apportionment of PAHs in atmospheric aerosol, soil and more recently surface sediments (Stout and Graan, 2010; Lin et al., 2011; Gao et al., 2013; Fang et al., 2016; Hu et al., 2017). Applying PMF model to sediment core research make it possible to quantitatively obtain the temporal variations of different sources, which affords the probability to evaluate the accumulated effectiveness of past-century political decisions on changing fuel strategy and other mitigation efforts. While it should be noted that there is no guarantee for optimized results of PMF output. For example, the critical selection of the number of PMF factors is largely affected by the experience of users. Therefore, model validation and additional environmental forensics are vital to ensure a successful PMF analysis. The similar combustion source of PAHs and Pb inspired us to test whether the integrated methods of PAHs signatures and Pb isotopic ratios show intersections in their source apportionment results, which in turn allowed for possible complementation and cross-confirmation from different perspectives.

The South China Sea is the largest marginal sea in the western Pacific with a deep semi-closed basin and wide continental shelves. The northern South China Sea (NSCS) is close to one of the most densely populated and economically dynamic regions, notably the Pearl River Delta. This has resulted in significant air and water pollution (Mai et al., 2002; Fu et al., 2003). Contaminants from the Pearl River Delta may enter the Pearl River Estuary and the NSCS through surface runoff. The NSCS is also characterized with a monsoon climate, having stronger northeasterly winds prevailing in winter and relatively weak southwesterly winds in summer, which bring air pollutants from China and southeastern Asia, respectively (Yang et al., 2014). There is no doubt that the NSCS receive large loads of pollutants. On the other hand, the year-round relatively high temperatures in this region could turn the NSCS into an important source of pollutants to the global environment, as a result of the global distillation (Wania and Mackay, 1995). Therefore, pollutant deciphering and source identification of PAHs and Pb in the NSCS are issues of great concern to the public. To date, simultaneous information about the PAHs and Pb in the NSCS is sparse. Moreover, despite the common conclusion that coal and biomass burning are major sources of PAHs in the NSCS with DRs (Peng et al., 2008; Liu et al., 2012a). Their relative contribution and historical change remained unclear.

The main objective of this study thus are (i) to use PAHs and Pb as a multi-indicator approach to get spatial and temporal trends of pollutants in NSCS; (ii) to build integrated multi-methodologies of PAH compositions, diagnostic ratios, Pb isotopic ratios, and PMF model to further improve source apportionment from step-down technique and cross-confirmation perspective, and finally get quantitative information about the evolving pyrogenic sources. Due to the resolution of Pb stable isotopes and limited surface sediment samples, combined source identification was not conducted for surface samples here.

2. Materials and methods

2.1. Sampling

16 surface samples and one sediment core (55 cm) were collected in the NSCS on the R/V SHIYAN III in 2013 and 2014. The top 0–2 cm layers were carefully collected with a stainless steel spoon. Detailed sampling information was given in supporting information (SI) Table S1. The sampling site of the core (Station A; 18°57.628′N, 110°50.469′E; seawater depth of 88 m) is adjacent to the east of Hainan Island (Fig. 1a), which is one of the largest islands in China.

The samples were frozen at −18 °C until analysis. Before analysis, the thawed sediment core was sliced into 0.5 cm sections from 0 to 11 cm depth and 1 cm sections from 11 cm to the bottom depth of