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Research article

Transport and fluxes of terrestrial polycyclic aromatic hydrocarbons in a small mountain river and submarine canyon system

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ABSTRACT

Polycyclic aromatic hydrocarbon (PAH) concentrations in the Gaoping River were investigated in the wet and dry seasons. PAH characteristics allowed us to trace the particulate matter transported in a river-sea system containing a small mountain river, continental shelf, and submarine canyon. PAH signatures of the Gaoping River showed that particles were rapidly transported from the high mountain to the Gaoping coastal areas in the wet season, even arriving at the deep ocean via the Gaoping Submarine Canyon. By contrast, in the dry season, the particles were delivered quite slowly and included mostly pyrogenic contaminants. The annual riverine flux estimates for PAHs were 2241 kg in the Gaoping river-sea system. Only 18.0 kg were associated with the dissolved phase; the rest was bound onto particles. The fluxes caused by typhoons and their effects accounted for 20.2% of the dissolved and 68.4% of the particulate PAH fluxes from the river. Normalized partition coefficients for organic carbon suggested that PAHs were rigid on the particles. Distinct source characteristics were evident for PAHs on riverine suspended particles and coastal surface sediments: the particles in the wet season (as background signals) were similar to petrogenic sources, whereas the particles in the dry season had characteristics of coal burning and vehicular emissions. The sediments in the northwestern shelf were similar to pyrogenic sources (including vehicular emissions and coal and biomass burning), whereas the sediments in the canyon and southeastern shelf arose from mixed sources, although some diesel signature was also evident.

1. Introduction

Oceans are the terminal sinks for organic matter derived from both marine and land-based sources and are key players in the global carbon cycle (Hedges and Oades, 1997). Organic carbon in the coastal environment is mainly derived from terrestrial matter via river runoff, coastal erosion, and aeolian transport (Zeng et al., 2004, and references therein). Therefore, delivery by rivers is one of the primary factors affecting organic matter in coastal ecosystems, especially near river mouths (Sanchez-Vidal et al., 2013).

Riverine dissolved organic carbon (DOC) and particulate organic carbon (POC) can supply organic carbon that materializes in seawater and sediments (Hedges et al., 1997; Selvaraj et al., 2015). The wide ranges of POC and DOC compounds make them the most important carriers of nutrients and organic contaminants (e.g., polycyclic aromatic hydrocarbons, PAHs) in the aqueous environment. Tropical cyclones (typhoons or hurricanes) and concentrated rainfall are the most important drivers that introduce terrestrial materials into the oceans (Hilton et al., 2008). The increasing frequency and intensity of extreme climatic events, including strong cyclones and high intensity rainfall in the river catchments, may trigger floods, debris floods, or debris flows that can carry enormous amounts of terrestrial materials toward the ocean (Borga et al., 2014; IPCC, 2012; Liu et al., 2016).

PAHs are noted for their potential toxicity, carcinogenic, and

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mutagenic effects, and they pose a significant ecological threat to the coastal environment (Amarillo et al., 2014; Lemieux et al., 2015). PAHs persist in the environment and can therefore be transported via oceanic and atmospheric circulation to areas quite remote from the regions where they are produced or used (Zhao et al., 2015). Their specific patterns of distribution and diagnostic ratios allow them to serve as reliable tracers for exploring the fate of particles. In addition, PAHs have high affinity for organic carbon and soot carbon (Thorsen et al., 2004), a physical characteristic that affects their distributions and effects on the environment.

The Gaoping River (GPR) is a typical small mountain river with a steep gradient (1/150) over the short distance from its headwater to the confluence or mouth (Liu et al., 2006, 2009; Milliman and Syvitski, 1992). The riverine particle flux ranges from 36 to 49 Mt a^{-1} (Mt, megatonne or 10^{12} g), but is, by comparison, only 5% and 10% that of Yellow and Yangtze Rivers, respectively (Dadson et al., 2003; Milliman and Kao, 2005; Milliman and Meade, 1983; Water Resources Agency, 1997). Extremely high annual particle fluxes were observed in all these rivers in the wet season (Gaoping River 95%, Yellow River 92%, and Yangtze River 93%) (Chen et al., 2001; Gao et al., 2015; Liu et al., 2013). Most particles with POC and adsorbed contaminants are delivered into the Gaoping coastal waters, especially via the Gaoping Submarine Canyon (Hsu et al., 2014; Sparkes et al., 2015). These substances can subsequently be transported to the South China Sea or the branch of the Kursoshio current that passes through the Taiwan Strait northward to Japan. Liu et al. (2013) and Kao et al. (2014) pointed out that episodic events are the major drivers and deliver most of the terrestrial materials to the sea from small mountain rivers. These events introduce large quantities of organic matter and contaminants in a short time, but few studies have attempted to estimate their fluxes.

Some studies have examined PAHs in the GPR or coastal waters (Doong and Lin, 2004; Fang et al., 2007, 2009; Jiang et al., 2009), but the transport and fate of PAHs in a river-sea dispersal system have not been fully documented. Taiwan's tropical and subtropical climate means that tropical cyclones (typhoons) frequently lash its landmass, allowing the export of terrestrial materials and contaminants into oceans during episodic events. The increasing frequency and intensity caused by extreme climatic events (IPCC, 2012) emphasizes the importance of studying the export of these compounds when addressing these episodic events.

The objective of the present study was therefore to investigate the fluxes and fates of PAHs and organic carbon in the GPR during both wet and dry seasons. The i*n situ* partition behavior of PAHs between the dissolved and particulate phases was also studied. In addition, since PAHs can serve as a potential material for distinguishing the sources and sinks in a river-sea system, riverine suspended particles (*RSP*s) were compared with coastal surface sediments (*CSS*s) to explore the transport and fate of particulate matter in this system. The dispersion of terrestrial materials in the river-sea system was therefore revealed by the PAH chemical tracers. Fluxes under extreme weather conditions could also provide valuable information for risk assessment under a changing climate.

2. Material and methods

Water samples in the GPR were collected on a monthly basis, from November 2006 to November 2007, except during flooding after typhoons in August and September 2007. The sampling location was located just before the tidal reach of the river, where the salinity was less than 0.1 (Fig. 1). The sampling and analytical procedures were adapted from previous methods (Fang et al., 2008, 2012) and are described only briefly here. The water samples (20 L) were pumped through Teflon tubing into stainless steel containers

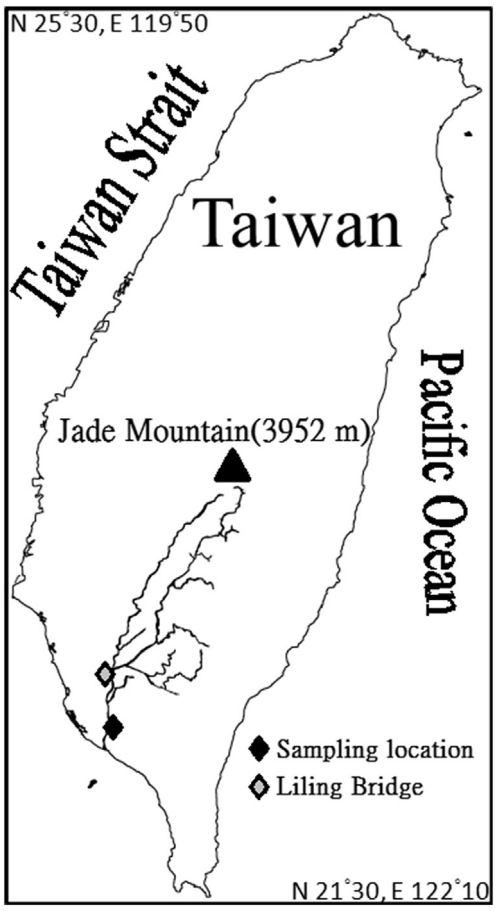

Fig. 1. A map of the sampling locations in the Gaoping catchment.

within 15 min. The particulate and dissolved samples were separated with glass fiber filters (0.7 μm, diameter 293 mm) and the dissolved samples were adsorbed onto Amberlite XAD-2 resin (Supelco). After pretreatment, the collected samples were subjected to the following procedures: Soxhlet extraction, liquid-liquid extraction, clean-up, and concentration. Organic matter [POC, Black carbon (BC) and total nitrogen (TN)] was measured with an elemental analyzer (Vario EL III; Hanau, Germany) and DOC with a TOC Analyzer (Aurora 1030, OI Analytical/Xylem Inc). Twenty-eight PAHs (Table 1) were identified and quantified by capillary gas chromatography (Agilent 6890) and mass spectrometry (Agilent 5973N; operated in selected ion-monitoring mode). Immediately prior to analysis, a mixture of five perdeuterated PAHs [acenaphene-D_{10}, phenanthrene-D_{10}, benzo(*a*)anthracene-D_{10}, benzo(*a*)pyrene-D_{12}, and benzo(*g*,*h*,*i*)perylene-D_{12}] was added to each extract as an internal standard. Each PAH was identified by its retention time relative to the internal standards and quantified by comparing the integrated area of the molecular ion chromatogram with that of the internal standard.

A mixture of four perdeuterated PAHs (naphthalene-D_8, fluorene-D_{10}, fluoranthene-D_{10} and perylene-D_{12}) was added to each sample prior to extraction as a surrogate to monitor the performance of the overall analytical procedure. The average recoveries were 55.8 ± 10.1, 81.3 ± 11.2, 66.6 ± 8.57, and 63.0 ± 10.1% in the dissolved phase and 64.2 ± 8.79, 90.6 ± 4.70, 85.6 ± 8.40, and 93.0 ± 15.8% in the particulate phase, for naphthalene-D_8, fluorene-D_{10}, fluoranthene-D_{10}, and perylene-D_{12}, respectively. PAH concentrations presented in this study were not corrected for surrogate recoveries to avoid overestimation.