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.

Keywords:

Gaoping River (Taiwan), Organic Carbon, Typhoon, Partition Coefficient, Source to Sink.

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 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., 2009; Liu et al., 2006; Milliman and Syvitski, 1992). The riverine particle flux ranges from 36–49 Mt a⁻¹ (Mt, megatonne or 10¹² 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 Kuroshio 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., 2009; Fang et al., 2007; 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 *in 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 (*RSPs*) were compared with coastal surface sediments (*CSSs*) 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; Fang et al., 2012) and are described only briefly here. The water samples (20 L) were pumped through Teflon tubing into stainless steel containers within 15 minutes. The particulate and dissolved samples were separated with glass fiber filters (0.7 μ m, 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-D₁₀, phenanthrene-D₁₀, benzo(a)anthracene-D₁₀, benzo(a)pyrene-D₁₂, and benzo(g,h,i)perylene-D₁₂] 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-D₈, fluorene-D₁₀, fluoranthene-D₁₀ and perylene-D₁₂) 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-D₈, fluorene-D₁₀, fluoranthene-D₁₀, and perylene-D₁₂, respectively. PAH concentrations presented in this study were not corrected for surrogate recoveries to avoid overestimation.

Water discharge [daily, m³ s⁻¹, Water Resources Agency (2007, 2008)] and total suspended solid concentrations in the GPR are presented in Figure 2 and Table 2. The monthly discharge in this study indicated a dry season from January to April 2007, a wet season from June to October 2007, and other periods indicating a seasonal transition with dry and/or wet signatures.

3. Results and discussion

3.1 Organic carbon and total nitrogen

DOC concentrations (mg C L⁻¹) were higher in the dry season than in the wet season (Fig. 2c). The concentrations of particulate materials (POC, AOC, BC, and TN, Figs. 2 b, d, and e) showed a significant relationship with the total suspended solid concentrations (Table 3) and were higher in the wet season than in the dry season. In contrast, their fractions of the particles, POC and TN fractions (%) (Fig. 2f), were lower in the wet season than in the dry season and

increased to a high level right after the wet season or typhoons (November 2006, December 2006, and November 2007), indicating that the POC and TN fractions could be affected by *in situ* production.

The BC fractions (%) were higher in the dry season than in the wet season (Fig. 2g). BC, which is a specific form of soot carbon arising from pyrogenic sources, shows a higher absorption capacity for organic contaminants than is seen with other amorphous forms of organic carbon (AOC) (Cornelissen and Gustafsson, 2003; Cornelissen et al., 2004). Interference from anthropogenic sources was minimized by separating AOC from POC (where the POC fraction is the sum of the BC and AOC fractions). The AOC fraction (%) was quite close in value to POC fraction, as the BC fraction only accounted for a small proportion of the total.

The geology in the catchment is largely sedimentary, with a low C/N ratio, so the C/N ratio is not a suitable indicator for distinguishing terrestrial from marine origins (Hilton et al., 2010; Selvaraj et al., 2015). Organic nitrogen was not measured in this study, but the molar POC/TN ratio could still be helpful in identifying particulate sources (Hung et al., 2012). The molar POC/TN ratios were lower in the wet season (5.28, 5.69, and 5.83) than in other seasons (6.08–7.39) (Fig. 2h). The sources of particles in the wet season seemed to be similar, as they shared this ratio.

3.2 PAH concentrations in the GPR

PAH concentrations in both the dissolved (C_D) and particulate phases (C_P) showed seasonal variations and were affected by water discharge or total suspended solid concentrations (Figs. 3 a and b). C_D accounted for $64.0 \pm 4.97\%$ of total PAH concentrations (dissolved and particulate phases) in the dry season, whereas C_P accounted for $95.2 \pm 3.7\%$ in the wet season and occurred

together with high total suspended solid concentrations. Extremely low C_D (0.42 ng L^{-1}) and high C_P (123 ng L^{-1}) levels were measured at extremely high water discharge ($768 \text{ m}^3 \text{ s}^{-1}$), because the total suspended solid concentration was high (758 mg L^{-1}) on the fifth day after a typhoon. Several studies also found that C_P was much higher in a storm flow than in a base flow (Blanchard et al., 2001; Foster et al., 2000; Hwang and Foster, 2006). C_D showed a significant linear positive correlation with DOC concentrations ($r=0.857$ and $p=0.0007$, Table 4). The higher DOC concentrations resulted in a higher detection frequency of dissolved high molecular weight PAHs (molecular weight ≥ 252), which were almost below the detection limits in the wet season.

C_P was significantly correlated with total suspended solid concentrations ($r=0.931$ and $p=0.00003$, Table 3). C_P was transformed to C_S (ng g^{-1}) (normalized by total suspended solid concentrations) representing the PAH mass on the particles to estimate PAHs adsorbed onto the particles (Fig. 3c). C_S ranged from 209–892, 131–367, and 351–713 ng g^{-1} , in the transition season, the wet season, and the dry season, respectively. C_S had a significant linear positive correlation with the POC ($r=0.684$ and $p=0.020$) and AOC fractions ($r=0.673$ and $p=0.023$) (Table 3). The relationship between C_S and BC fractions was not significant, although particles with higher BC fractions were associated with higher C_S .

Three sediment quality guidelines—the *Effects Range-Low/Effects Range-Medium* of the National Oceanographic and Atmospheric Administration, the *Threshold Effects Level/Probable Effects Level* of the Florida Department of Environmental Protection, and the upper limit/lower limit of the Taiwan Environmental Protection Administration (Table 5)—were used to assess the PAH risk in the aqueous environment (Long et al., 1995; MacDonald et al., 1996; Taiwan Environmental Protection Administration). Briefly, C_S values higher than the *Effects Range-Low*, the *Threshold Effects Level*, or the lower limit indicate situations should trigger interest. If values

are higher than the *Effects Range-Medium, Probable Effects Level*, or the upper limit, living things might be harmed so the remedial action might be necessary.

All the C_S values were lower than the *Effects Range-Medium, Probable Effects Level* and lower limit. One fluorene concentration was higher than the *Effects Range-Low and Threshold Effects Level*; two phenanthrene concentrations and one dibenzo[a,h]anthracene concentration were higher than the *Threshold Effects Level*. Except for one phenanthrene value in April 2007, concentrations higher than the sediment quality guidelines were noted in the transition season, which had high POC fractions. Thus, the particles having high organic carbon fractions should be of concern because of potential adverse influences in the aqueous environment.

PAH concentrations (C_D , C_P , and C_S) in the GPR were the same or relatively lower when compared with those in other rivers (Table S1), such as the Jinjiang River (Yang et al., 2013), the Seine and its estuary (Fernandes et al., 1997; Gateuille et al., 2014), the Susquehanna River (Ko and Baker, 2004), the Henan Reach of the Yellow River (Sun et al., 2009), the Sarno River (Montuori and Triassi, 2012), the Pearl River (Wang et al., 2007), the Pawtuxet River (Cantwell et al., 2014), the Chenab River (Farooq et al., 2011), and the Anacostia River (Hwang and Foster, 2006). The C_D values observed in this study were significantly lower than those reported by Doong and Lin (2004), also from the GPR. This difference could be due to the extremely high naphthalene concentrations ($30 - 9,100 \text{ ng L}^{-1}$) measured by Doong and Lin which were not determined in the present study.

3.3 The partition between the dissolved and particulate phases

PAH partitioning between solids and water is an important consideration when investigating the transport and fate of hydrophobic organic pollutants in an aqueous environment.

The partition coefficient between the particulate and dissolved phases (K_P) is:

$$K_P (\text{L kg}^{-1}) = C_S / C_D \quad (1)$$

In addition, POC is used to normalize K_P :

$$K_{OC} (\text{L kg}^{-1}) = K_P / f_{POC} \quad (2)$$

where K_{OC} is the organic carbon normalized partition coefficient and f_{POC} is POC fraction. The *in situ* $\log K_{OC}$ was calculated and compared to the experimental $\log K_{OC}$ predicted by $\log K_{OW}$ (Fig. 4) (Means et al., 1980). The *in situ* $\log K_{OC}$ in the wet season was much higher than that predicted by $\log K_{OW}$. The extremely low C_D in the wet season caused the high *in situ* $\log K_{OC}$ values calculated in this study. In other seasons, the *in situ* $\log K_{OC}$ had a significant relationship with $\log K_{OW}$ when $\log K_{OW}$ was less than 6.2 ($\log K_{OC} = 0.72 \log K_{OW} + 2.34$, $R^2 = 0.91$, $p < 0.0001$). If this relationship is applied to samples with $\log K_{OW} > 6.2$, their C_D values should be under the detection limits. Most of these high molecular weight PAHs in the dissolved phase were only measured with high DOC concentrations in the dry season. The *in situ* $\log K_{OC}$ with $\log K_{OW} > 6.2$ (benzo[e]pyrene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-c,d]pyrene) showed poor agreement with the $\log K_{OC}$ predicted from $\log K_{OW}$. Wu et al. (2011) found that K_P decreased from five-ring to six-ring PAHs and Qi et al. (2012) also found that the $\log K_{OC}$ of dibenzo[a,h]anthracene was lower than the $\log K_{OW}$ from some samples collected in the field. Moreover, colloidal organic carbon has been reported to enhance organic contaminant concentration in the aqueous environment (Burgess et al., 1996; Mitra and Bianchi, 2003; Mitra et al., 1999). The differences between truly dissolved, colloidal and fine-grained ($< 0.7 \mu\text{m}$) particles could also be a cause (Fernandes et al., 1997).

Although DOC enhanced the concentrations of organic compounds in the dissolved phase, a competitive adsorption mechanism between DOC and organic compounds has also been documented (Newcombe et al., 2002). The sorption of organic compounds to POC is related to the character of the POC, such as its chemical composition, molecular weight, solution chemistry, pore size distribution, surface chemistry, and pore structure (Kilduff et al., 1996; Wang et al., 2011); Low molecular weight organic compounds are most competitive, participating in direct competition with other high molecular weight organic compounds for adsorption sites (Quinlivan et al., 2005). This explains, in line with the findings of Wu et al. (2011) and Qi et al. (2012), why relatively low *in situ* $\log K_{OC}$ values were found for high molecular weight PAHs in this study, as these PAHs did not adsorb as effectively onto particles when compared to low molecular weight PAHs.

3.4 Source identification in the particulate phase

The high $\log K_{OC}$ values found in the GPR showed that PAHs tended to adsorb onto the particulates. Furthermore, the higher $\log K_{OC}$ than the experimental $\log K_{OC}$ predicted by $\log K_{OW}$ (Means et al., 1980) illustrated that PAHs were not readily released into the dissolved phase after adsorption onto particles. Thus, using particulate PAHs to trace sources is more reliable than using dissolved PAHs. The signatures of particulate PAHs can be used to determine possible sources of particles.

3.4.1 Biological signature

Perylene is usually used to identify the biogenic source from biogenic precursors during early diagenesis (Boonyatumanond et al., 2006; Silliman et al., 2000; Venkatesan, 1988).

Perylene from biogenic sources is highly abundant compared with the total penta-PAHs (benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, and perylene). A perylene/penta-PAH ratio higher than 0.1 suggests biogenic sources (Readman et al., 2002 and references therein), while a ratio less than 0.1 is attributed to pyrogenic sources (Baumard et al., 1998).

Perylene/penta-PAH ratios were higher in the dry season (0.46–0.57) than in the wet season (0.16–0.33). The *in situ* production, with diagenetic formation from terrestrial precursors, may contribute to the presence of perylene, especially at less contaminated locations (Venkatesan, 1988) or in tropical climates (Boonyatumanond et al., 2006). In the wet season, riverine suspended particles at high water discharge were directly transported from mountains to the sea and exhibited low perylene/penta-PAH ratios in the GPR. The particles transported into the Gaoping Submarine Canyon after typhoons also showed low ratios, from 0.07 to 0.13, as a background signal (Lin et al., 2013).

3.4.2 Diagnostic ratios

Several molecular ratios, such as anthracene/(anthracene+phenanthrene), fluoranthene/(fluoranthene+pyrene), benzo[a]anthracene/(benzo[a]anthracene+chrysene+triphenylene), and indeno[1,2,3-c,d]pyrene/(indeno[1,2,3-c,d]pyrene+benzo[g,h,i]perylene), have been used for source recognition (Rockne et al., 2002; Van Metre and Mahler, 2004; Yunker et al., 2002). Three ratios, fluoranthene/(fluoranthene+pyrene), benzo[a]anthracene/(benzo[a]anthracene+chrysene+triphenylene), and indeno[1,2,3-c,d]pyrene/(indeno[1,2,3-c,d]pyrene+benzo[g,h,i]perylene) have been successfully used to distinguish the possible sources along the south coast of Taiwan (Fang

et al., 2009; Fang et al., 2007; Jiang et al., 2009; Kuo et al., 2014; Lin et al., 2013) and were adopted for the particulate phase in this study.

The *RSPs* in the wet season were predominantly from petrogenic sources, while the dry season revealed a strong pyrogenic signal (Fig. 5). Notably, both ratios indicated an obvious pyrogenic signal for the sample collected in November 2006. This source of biomass burning signature could be the result of straw-burning activity that occurred along the river banks prior to sampling. Some precipitation occurred before the sampling in May 2007, causing samples to show wet season characteristics.

Diagnostic ratios in October 2007, after the typhoon, showed a clear petrogenic signal or low petroleum combustion (Fig. 5). Five days after the typhoon, particles with anthropogenic contaminants should have been washed out and the particles collected would have been derived from erosion of the mountain slopes during the typhoon. Thus, the natural particles showed ratios that were low and close to the petrogenic signature. This was also found for particles collected at the head of the Gaoping Submarine Canyon (Lin et al., 2013). Typhoons continued to affect Taiwan in October and November 2007, so the particles from November 2007 resembled those found in the wet season.

The particles in the wet season likely arose from similar sources, as they showed similar perylene/penta-PAH ratios and diagnostic ratios. Their C_S values were also relatively low. These results were close to those for the particles delivered from the GPR into the ocean after a typhoon, as a background signal (Lin et al., 2013). The particles with low C_S and high petrogenic signatures could be considered as the background signal in the GPR.

3.5 Riverine fluxes

3.5.1 Fluxes of discharge, total suspended solid, and organic carbon

At a given flow, total suspended solid concentrations could be estimated from the relationship between water discharge and total suspended solid concentrations, which most commonly is a power function (Jansson, 1997; Khanchoul and Jansson, 2008; Walling, 1978):

$$C_{TSS} = aQ^b \quad (3)$$

where C_{TSS} is total suspended solid concentration, Q is water discharge, and a and b are the regression coefficients. The particle flux at Liling Bridge was calculated based on the recorded data (total suspended solid concentration and water discharge) (Water Resources Agency, 2007, 2008). The particle flux at the sampling location was estimated based on the total suspended solid concentrations measured and the water discharge which was corrected from that obtained at Liling Bridge by the watershed area and precipitation (David, 2000) (details in the supplementary material).

The GPR exported 25.8 Mt a^{-1} particles from above Liling Bridge and at least 15.8 Mt a^{-1} was delivered into the estuary (sampling location) (Table 2). The strong typhoons, Sepat and Krosa, output 2.51 and 1.85 Mt particles (15.8 and 11.7% of the annual particle fluxes, Table 6) during periods of typhoon warnings. The differences in particle fluxes between Liling Bridge and the sampling locations were 64.3–65.5% in the dry season, 47.7–59.9% in other seasons, and 36.6–39.8% in the period with typhoon effects. These particles might be deposited in the lower reaches and be further washed out and exported in the wet season; some 61.0% water discharge and 87.6% particles arose during periods of typhoon warnings during this study. The beginnings of the two hyperpycnal turbidity currents showed strong pyrogenic signatures, followed later by petrogenic signatures (Lin et al., 2013). The pyrogenic signatures could suggest that the particles were deposited in the dry season within the river catchment.

DOC, POC, AOC, and BC concentrations were predicted from their relationships with water discharge or total suspended solid concentrations (Table 3) and the fluxes of organic carbon were estimated (Table 2). The sample from October 2007 on the fifth day after the typhoon could be considered as a background signal. These particles with low C_s and petrogenic signatures in the wet season were considered to represent the background signal of the GPR after thorough washing out by the typhoon (Lin et al., 2013). If the values predicted were lower than the values in October 2007, they would be replaced by the background values. Most of these fluxes occurred in the high discharge period, especially during periods of typhoon warnings. The annual DOC flux was 6.74 kt a^{-1} in this study. The annual DOC flux was 84.2% in the wet season and the annual DOC flux affected by typhoons was 40.1%. Although DOC flux only accounted for a small proportion of the world total, DOC yield ($2.07 \text{ t km}^{-2} \text{ a}^{-1}$) in the GPR was higher than the average DOC yields of global rivers [$1.9 \text{ t km}^{-2} \text{ a}^{-1}$, Ludwig et al. (1996)], the Yellow River [$0.1\text{-}0.3 \text{ t km}^{-2} \text{ a}^{-1}$, Zhang et al. (1992); Cauwet and Mackenzie (1993)] and the Yangtze River [$0.5 \text{ t km}^{-2} \text{ a}^{-1}$, Wu et al. (2007)].

The annual POC flux was 94.4 kt a^{-1} , including 89.6 Kt a^{-1} AOC and 4.83 kt a^{-1} BC. The annual POC flux in the wet season was 99.3% and was 86.7% during the periods of typhoon warnings. As is typical for small mountain rivers, the particle and POC yields in the Gaoping watershed were higher than those reported for other important rivers in the world, such as the Amazon and Changjiang Rivers (Hung et al., 2012, and references therein). Particle and POC fluxes in the GPR were lower than those reported by Hung et al. (2012) (particle flux 37 Mt a^{-1} and POC flux 226 kt a^{-1}), due to sampling site differences between the two studies. A lower water velocity at the sampling location would promote an easier deposition of riverine suspended particles than at the WanTa Bridge, the sampling location in Hung's study.

3.5.2 PAH fluxes estimation

C_D and C_P were estimated using multiple linear regression models (details in the supplementary material):

$$\log C_D = -1.01 \log Q + 2.59 \quad (R^2 = 0.845 \text{ and } p < 0.001) \quad (4)$$

$$\log C_P = 0.627 \log C_{TSS} + 0.033 \log C_{AOC} + 0.010 \log C_{BC} + 0.257 \quad (p = 0.006) \quad (5)$$

in which C_{AOC} and C_{BC} are AOC and BC concentrations.

The estimated values had a significant linear relationship with the measured C_D ($R^2=0.730$, $p=0.0008$) and C_P ($R^2=0.774$, $p=0.0004$). Total annual PAH flux was 2241 kg, including 18.0 kg in the dissolved phase and 2223 kg in the particulate phase (Table 2). High water discharge, particle, and PAH fluxes mostly occurred in the wet season (June to October 2007) or were related to the typhoons (Table 6). Typhoons are the major drivers that export terrestrial matter to the ocean in this region.

Annual PAH fluxes in the GPR were significantly lower than most of other global rivers (Table S2). However, PAH yields ($\text{g km}^{-2} \text{ a}^{-1}$) in the GPR were not so that GPR only has a small catchment area. Dissolved PAH yield in the GPR and Ebro River (Lipiatou et al., 1997) were at the same level. Particulate PAH yield and total PAH yield were in the same order compared with Chenab River (Farooq et al., 2011), but were much higher than those from Susquehanna (Ko and Baker, 2004), Ebro (Lipiatou et al., 1997), Pawtuxet (Cantwell et al., 2014), Rhone (Bouloubassi et al., 2012; Lipiatou et al., 1997), Pearl, Yangtze, Yellow (Wang et al., 2007), and San Francisco (Greenfield and Davis, 2005) Rivers.

3.6 Hierarchical cluster analysis and principal component analysis

The sedimentation rate in the southern Taiwan coastal area is high during specific events, but low over a long time scale (Huh et al., 2009). This result is related to the extremely high sediment discharge from small mountain rivers and from the typhoons that frequently lash Taiwan (Liu et al., 2013). These discharges transport large amount of sediments to coastal areas, where they are temporarily deposited before subsequent removal and transport to the deep ocean. The Gaoping coast could therefore be considered to represent a sink for recent particles. Its coastal surface sediments (*CSSs*), as described by Fang et al. (2007), were compared with *RSPs* in the GPR by hierarchical cluster analysis and principal component analysis to reveal the fate of particles in the Gaoping Dispersal System.

Six clusters are recognized by hierarchical cluster analysis from *RSPs* and *CSSs* (Figs. 6, S1 and S2). The *RSPs* in November 2006 clustered alone as cluster 6, with high proportions of indeno[1,2,3-c,d]pyrene and dibenzo[a,h]anthracene; this could be a result of the nearby straw-burning activity already mentioned. Cluster 4 (four sediments, *CSSs* in the canyon and southeastern shelf II) was linked to diesel fuel from unburnt petrogenic sources (1-methylfluorene) and S-containing aromatic compounds (dibenzothiophene and 4,6-dimethyldibenzothiophene) (Fang et al., 2003; Yang et al., 1998; Zeng et al., 2004).

Clusters 1 (*CSSs* in the canyon and southeastern shelf I) and 2 (*RSPs* in the wet season) showed higher proportions of phenanthrene, 3-methylphenanthrene, and 2-methylphenanthrene than were found in clusters 3 (*CSSs* in the northwestern shelf) and 5 (*RSPs* in the dry season). Low molecular weight and methyl PAHs are related to petrogenic sources (Jiang et al., 2009;

Miki et al., 2014; Saha et al., 2009). Clusters 3 and 5 were identified as coal burning by the presence of higher proportions of fluoranthene and pyrene (Ribeiro et al., 2012; Ribeiro et al., 2014).

In addition to the different sources, other differences between *CSSs* and *RSPs* were found. The *CSSs* (clusters 1 and 3) had higher proportions in a few high molecular weight PAHs (benzo[a]fluorene, chrysene+triphenylene, benzo[b]fluoranthene, benzo[e]pyrene, indeno[1,2,3-c,d]pyrene, benzo[g,h,i]perylene and coronene) when compared to *RSPs* (clusters 2 and 5), which had higher proportions of low molecular weight PAHs (anthracene, 2-methylanthracene and 1-methylphenanthrene). Biomass burning and vehicular emission (from atmospheric deposition or road washing with rainfall) could be the sources that produced these high molecular weight PAHs in *CSSs* (Yunker et al., 2002).

Principal component analysis extracted six components from *RSPs* and *CSSs*. Each component was extracted with the correlation matrix eigenvalues more than 1. Here, we only discuss the first four components, accounting for 23.2, 20.5, 19.0, and 9.7% (Table S3). The fourth component is only used to explain the straw burning (biomass burning) in November 2006.

PC1 and PC2 identified three groups (Fig. 7a), similar to the hierarchical cluster analysis results. Group 1 (clusters 2 and 5) showed *RSPs* with high loading in low molecular weight PAHs (anthracene, pyrene and 2-methylanthracene) as petrogenic sources; Group 2 (clusters 1 and 3) indicated most *CSSs* with high loading in high molecular weight PAHs (benzo[a]fluorene, chrysene+triphenylene, benzo[e]pyrene, benzo[g,h,i]perylene, and coronene) from biomass burning and vehicular emission; Group 3 (cluster 4) showed four sediments with both low molecular weight PAHs (anthracene, pyrene and 2-methylanthracene) and diesel signal (dibenzothiophene, 1-methylfluorene, 4,6-dimethyldibenzothiophene, and 3,6-

dimethylphenanthrene). The *RSPs* had a higher petrogenic signature; the *CSSs* had a higher pyrogenic signature in PC1 and the diesel signal was displayed by PC2.

PC1 and PC3 further illustrated the difference between petrogenic and pyrogenic sources in greater detail (Fig. 7b). The *RSPs* in the dry season (cluster 5) and *CSSs* in the northwestern shelf (cluster 3) exhibited a higher loading of pyrogenic PAHs (fluoranthene, benzo[a]anthracene, benzo[b]fluoranthene, and benzo[a]pyrene), from coal burning and vehicular emission, than of other compounds in PC3. The *RSPs* in the wet season (cluster 2) had high abundance of methyl phenanthrene (3-methylphenanthrene, 2-methylphenanthrene, and 1-methylphenanthrene) and *CSSs* in the canyon and southeastern shelf (cluster 1) were mixed sources when compared to the others.

3.7 Fate of particles in the Gaoping Dispersal System

In this study, the particles in the wet season included: (1) the particles deposited in the catchment before, and (2) the particles derived from erosion of the mountain slopes during the typhoon and heavy rainfall. The Taiwan mountains were under the sea millions of years ago. The eroded particles episodically delivered into the sea in the wet season were older than the existing marine particles (Liu et al., 2016).

Hierarchical cluster analysis and principal component analysis results showed the different characters of PAH sources in the Gaoping Dispersal system. The *RSPs* in the wet season were dominated by low molecular weight and methyl PAHs as petrogenic markers. This characteristic of low PAH concentrations can be considered as the background signal. The *RSPs* in the dry season had few low molecular weight PAHs were classified as a pyrogenic signal from

coal burning and vehicular emission. The CSSs in the northwestern shelf showed a greater contribution from pyrogenic sources than RSPs in the dry season, which included coal burning, biomass burning and vehicular emission. The sources of CSSs in the canyon and southeastern shelf were of two types: unburnt diesel fuel and mixed sources. The signature of biomass burning decreased from the north to south shelf, implying the transport of pyrogenic particles.

4. Conclusions

Much of the annual water discharge and particle fluxes arose in the wet season due to typhoons and heavy rainfall. Enormous quantities of organic substances were also exported with this water discharge and attached to particles. C_D was diluted by the water discharge and C_P varied with total suspended solid concentrations. PAH concentrations showed significant correlations with DOC and POC, indicating the importance of organic carbon to PAHs. Particles with high POC fractions should be further investigated to avoid the possible adverse effects, since the concentrations of fluorine, phenanthrene, and dibenzo[a,h]anthracene were higher than the values of the *Effects Range-Medium* and the *threshold effects level*. The annual riverine PAH flux (November 2006 to October 2007) was 2241 kg, including 18.0 kg in the dissolved phase and 2223 kg in the particulate phase. In October 2007, the major contribution from a single typhoon, Krosa, accounted for 5.51% and 14.7% of the annual dissolved and particulate PAH fluxes, respectively.

Particles collected on the fifth day after Typhoon Krosa showed very low diagnostic ratios, as a natural characteristic rather than petrogenic source. Petrogenic sources dominated in the wet season, with the same signal as the background signature, while the sources in the dry season were both pyrogenic and biogenic. The hydrophobic character affected PAH partitioning

in the system: the *in situ* $\log K_{OC}$ values in the dry season showed a significantly positive linear relationship with the $\log K_{OC}$ values predicted from $\log K_{OW}$ ($\log K_{OW} < 6.2$). DOC, AOC, BC, and colloid organic matter were all the factors that affected PAHs in the field.

Comparisons between *RSPs* and *CSSs* gave the following results: (I) particles in the wet season were petrogenic, and this character could be set as the background signal in the Gaoping catchment; (II) particles in the dry season were pyrogenic from coal burning and vehicular emissions; (III) sediments in northwestern shelf were pyrogenic, arising from vehicular emissions, coal burning, and biomass burning; (IV) sediments in the canyon and southeastern shelf were from mixed sources and a diesel signature was observed. Most particles with a petrogenic signature were discharged in the wet season and dispersed in the coastal area. However, the signature of sediments in the northwestern shelf indicated a predominance of pyrogenic sources, suggesting a significant anthropogenic input from the north side of the canyon. PAHs were successfully used in this study to infer the transport and fate of particles in the environment.

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Table Captions

Table 1 Polycyclic aromatic hydrocarbons (PAHs) analyzed in this study.

Table 2 Water discharge and total suspended solid (TSS) concentrations, and mass fluxes of particles, dissolved organic carbon (DOC), amorphous organic carbon (AOC), black carbon (BC), particulate organic carbon (POC), and polycyclic aromatic hydrocarbon (PAH) in the Gaoping River.

Table 3 Correlation matrix of (a) total suspended solid concentration (C_{TSS}), PAH concentration in the particulate phase (C_P), and concentrations of particulate organic carbon (POC), amorphous organic carbon (AOC), black carbon (BC), and total nitrogen (TN) (C_{POC} , C_{AOC} , C_{BC} , and C_{TN}), and (b) C_{TSS} , PAH concentrations on the particles (C_S), and fractions of POC, AOC, BC, and TN (F_{POC} , F_{AOC} , F_{BC} , and F_{TN}).

Table 4 Correlation matrix of water discharge (Q), polycyclic aromatic hydrocarbon concentration in the dissolved phase (C_D), and dissolved organic carbon concentration (C_{DOC}).

Table 5 Sediment quality guidelines: the *Effects Range-Low/Effects Range-Medium* (ERL/ERM) of the National Oceanographic and Atmospheric Administration (NOAA), the *Threshold Effects Level/Probable Effects Level* (TEL/PEL) of the Florida Department of Environmental Protection (FDEP) and the upper limit/lower limit (UL/LL) of the Taiwan Environmental Protection Administration (TW EPA).

Table 6 The proportions of annual fluxes in the wet season and during typhoons.

Figure Captions

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

Figure 2 (a) Water discharge, (b) total suspended solid (TSS) concentrations in the Gaoping River and the results of riverine organic analyses: (c) dissolved organic carbon (DOC) concentrations, (d) particulate organic carbon (POC) concentrations, (e) black carbon (BC) and total nitrogen (TN) concentrations, (f) POC and TN fractions, (g) BC fraction, and (h) the molar POC/TN ratio (Black symbols: dry season, white symbols: wet season and gray symbols: transition season).

Figure 3 (a) Polycyclic aromatic hydrocarbon (PAH) concentrations in the dissolved phase (C_D) and water discharge, (b) PAH concentrations in the particulate phase (C_P) and total suspended solid (TSS) concentrations and (c) PAH concentrations on the particles (C_S) in the Gaoping River.

Figure 4 Comparison of $\log K_{OW}$ and *in situ* $\log K_{OC}$ measured in the Gaoping River.

Figure 5 Diagnostic ratios of (a) fluoranthene/(fluoranthene+pyrene) ($Flt/(Flt+Py)$) vs. benzo[a]anthracene/(benzo[a]anthracene +chrysene+triphenylene) ($BaA/228$), and (b) indeno[1,2,3-c,d]pyrene/(indeno[1,2,3-c,d]pyrene+benzo[g,h,i]perylene) ($IP/(IP+BghiP)$) vs. $BaA/228$. The indeno[1,2,3-c,d]pyrene concentration in November 2007 was under the detection limit ($IP/(IP+BghiP) = 0$) and that is shown to compare $BaA/228$ with the other samples in Fig. 5b.

Figure 6 Polycyclic aromatic hydrocarbon (PAH) composition distributions of the results of hierarchical cluster analysis from the riverine suspended particles and coastal surface sediments.

Figure 7 Score plots of the first three principal components [(a) PC1 versus PC2 and (b) PC1 versus PC3] for polycyclic aromatic hydrocarbons in the riverine suspended particles and coastal surface sediments.

Table Captions (Supplementary material)

Table S1 Comparison of polycyclic aromatic hydrocarbon (PAH) concentrations [in the dissolved phase (C_D), in the particulate phase (C_P) and on the particles (C_S)] reported for various parts of the world.

Table S2 Comparison of polycyclic aromatic hydrocarbon (PAH) fluxes and yields reported for various parts of the world.

Table S3 Principal component analysis rotated component loadings of polycyclic aromatic hydrocarbons (PAHs) in the riverine suspended particles and the coastal surface sediments.

Figure Captions (Supplementary material)

Figure 1 Dendrogram of hierarchical cluster analysis.

Figure 2 Polycyclic aromatic hydrocarbon (PAH) composition distributions of each cluster of hierarchical cluster analysis from the riverine suspended particles and coastal surface sediments.

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Table 1 Polycyclic aromatic hydrocarbons (PAHs) analyzed in this study.

NO.	PAH compound	Abbreviation
01	Fluorene	Fluo
02	1-methylfluorene	1MeF
03	Dibenzothiophene	DBT
04	Phenanthrene	Ph
05	Anthracene	An
06	3-methylphenanthrene	3MeP
07	2-methylphenanthrene	2MeP
08	2-methylanthracene	2MeA
09	4,5-methylenephenanthrene	45MeP
10	1-methylphenanthrene	1MeP
11	4,6-dimethyldibenzothiophene	46DMD
12	3,6-dimethylphenanthrene	36DMP
13	Fluoranthene	Flt
14	Pyrene	Py
15	Benzo[a]fluorene	BaFl
16	Benzo[b]fluorene	BbFl
17	Benzo[a]anthracene	BaA
18,19	Chrysene+Triphenylene	Chry+TriPhe
20	Benzo[b]fluoranthene	BbFa
21	Benzo[k]fluoranthene	BkFa
22	Benzo[e]pyrene	BePy
23	Benzo[a]pyrene	BaPy
24	Perylene	Pery
25	Indeno[1,2,3-c,d]pyrene	IP
26	Dibenzo[a,h]anthracene	DBA
27	Benzo[g,h,i]perylene	BghiP
28	Coronene	Coro

Table 2 Water discharge and total suspended solid (TSS) concentrations, and mass fluxes of particles, dissolved organic carbon (DOC), amorphous organic carbon (AOC), black carbon (BC), particulate organic carbon (POC), and polycyclic aromatic hydrocarbon (PAH) in the Gaoping River.

Year	2006		2007											Annual flux Nov. 06 ~ Oct. 07
Month	Nov.	Dec.	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	
Season*	TS	TS	D	D	D	D	TS	W	W	W	W	W	TS	
Water discharge ($\text{m}^3 \text{S}^{-1}$) ^{a,b}	60	58	11	10	9	8	10	188	69	—	—	768	67	
TSS concentration (mg L^{-1}) ^{a,c}	52	27	36	24	46	29	40	402	206	—	—	758	9	
Riverine fluxes														
Monthly discharge ($\text{m}^3 \text{S}^{-1}$) ^b	1720	1630	347	218	223	289	1150	4540	4680	53,800	21,300	23,100	2650	113,000
Particle (measured, Kt, 10^9g) ^c	16.6	14.8	0.98	0.467	0.452	0.766	17	125	105	11,300	1380	2890	40.7	15,800
Particle (WRA, Kt, 10^9g) ^b	41.2	36.9	2.89	1.43	1.4	2.27	38.8	264	229	17,800	2600	4800	93.6	25,800
DOC (Kt, 10^9g)	0.274	0.268	0.102	0.073	0.077	0.088	0.181	0.473	0.507	2.1	1.31	1.27	0.35	6.73
AOC (Kt, 10^9g)	0.202	0.185	0.022	0.012	0.012	0.018	0.158	0.889	0.826	63.2	7.73	16.3	0.385	89.6
BC (Kt, 10^9g)	0.014	0.013	0.002	0.001	0.001	0.001	0.01	0.053	0.054	3.39	0.414	0.879	0.025	4.83
POC (Kt, 10^9g) ^d	0.216	0.199	0.024	0.013	0.013	0.019	0.169	0.943	0.877	66.6	8.14	17.2	0.41	94.4
Dissolved PAHs (Kg)	1.17	1.19	0.797	0.654	0.708	0.733	0.939	1.44	1.53	4.13	2.24	2.46	1.29	18.0
Particulate PAHs (Kg)	5.09	4.62	0.464	0.243	0.239	0.366	4.29	25.8	23.6	1537	218	404	10.4	2223

* TS: transition season, D: dry season and W: wet season

a Data in the sampling date

b Liling/Wanda Bridge, Water Resources Agency (2007, 2008)

c Measured at sampling location just before the tidal river reached

d POC flux is sum of AOC and BC fluxes.

— Samples were not collected.

Table 3 Correlation matrix of (a) total suspended solid concentration (C_{TSS}), PAH concentration in the particulate phase (C_P), and concentrations of particulate organic carbon (POC), amorphous organic carbon (AOC), black carbon (BC), and total nitrogen (TN) (C_{POC} , C_{AOC} , C_{BC} , and C_{TN}), and (b) C_{TSS} , PAH concentrations on the particles (C_S), and fractions of POC, AOC, BC, and TN (F_{POC} , F_{AOC} , F_{BC} , and F_{TN}).

(a)	C_{TSS}	C_P	C_{POC}	C_{BC}	C_{AOC}	C_{TN}	(b)	C_{TSS}	C_S	F_{POC}	F_{BC}	F_{AOC}	F_{TN}
C_{TSS}	1	0.931**	0.819**	0.940**	0.803**	0.848**	C_{TSS}	1	-0.608*	-0.528	-0.612*	-0.513	-0.520
C_P		1	0.685*	0.854**	0.669*	0.701*	C_S		1	0.684*	0.520	0.673*	0.673*
C_{POC}			1	0.745**	0.999**	0.991**	F_{POC}			1	0.174	1.000**	0.998**
C_{BC}				1	0.723*	0.774**	F_{BC}				1	0.148	0.174
C_{AOC}					1	0.989**	F_{AOC}					1	0.998**
C_{TN}						1	F_{TN}						1

* $p < 0.05$ and ** $p < 0.01$.

Table 4 Correlation matrix of water discharge (Q), polycyclic aromatic hydrocarbon concentration in the dissolved phase (C_D), dissolved organic carbon concentration (C_{DOC}).

	Q	C_D	C_{DOC}		logQ	log C_D	log C_{DOC}
Q	1	-0.531	-0.486	logQ	1	-0.921**	-0.896**
C_D		1	0.857**	log C_D		1	0.784**
C_{DOC}			1	log C_{DOC}			1

* p<0.05 and ** p<0.01.

Table 5 Sediment quality guidelines: the *Effects Range-Low/Effects Range-Medium* (ERL/ERM) of the National Oceanographic and Atmospheric Administration (NOAA), the *Threshold Effects Level/Probable Effects Level* (TEL/PEL) of the Florida Department of Environmental Protection (FDEP) and the upper limit/lower limit (UL/LL) of the Taiwan Environmental Protection Administration (TW EPA).

Concentration (ng g ⁻¹)	NOAA ^a		FDEP ^b		TW EPA ^c	
	<i>ERL</i>	<i>ERM</i>	<i>TEL</i>	<i>PEL</i>	LL	UL
Fluorene	19	540	21.2	144	40	260
Phenanthrene	240	1500	86.7	544	150	1120
Anthracene	84	1100	46.9	245	80	800
Fluoranthene	600	5100	113	1494	290	2860
Pyrene	665	2600	153	1398	290	2410
Benz[a]anthracene	261	1600	74.8	693	140	1210
Chrysene+Triphenylene	384	2800	108	846	190	1730
Benzo[a]pyrene	430	1600	88.8	763	160	1340
Dibenzo[a,h]anthracene	63.4	260	6.22	135	40	260

a Long et al., 1995.

b MacDonald et al., 1996.

c TW EPA (<http://www.epa.gov.tw/mp.asp?mp=epa>).

Table 6 The proportions of annual fluxes in the wet season and during typhoons.

		Typhoon warning*		Fluxes				
		Level*	Start	End	water discharge	particle	dissolved PAHs	particulate PAHs
Wet season (Jan-Oct 2007)					95.1%	99.7%	65.6%	99.3%
Six Typhoons					19.6%	29.0%	10.7%	27.6%
	Typhoon Pabuk	Light	2007/8/6 23:30	2007/8/8 14:30	1.46%**	0.61%**	1.35%**	0.70%**
	Typhoon Wutip	Light	2007/8/8 11:30	2007/8/9 11:30				
	Typhoon Sepat	Strong	2007/8/16 08:30	2007/8/19 14:30	8.84%	15.8%	4.00%	14.9%
	Typhoon Wipha	Middle	2007/9/17 05:30	2007/9/19 08:30	1.73%	0.80%	1.21%	0.89%
	Typhoon Krosa	Strong	2007/10/4 17:30	2007/10/7 23:30	7.29%	11.7%	3.36%	11.1%
	Typhoon Mitag	Middle	2007/11/26 05:30	2007/11/27 11:30	0.27%	0.049%	0.53%	0.075%
Typhoons and their effect					45.6%	70.7%	20.2%	68.4%

* Data from Central Weather Bureau, Taiwan

** Typhoons Pabuk and Wutip passed through Taiwan in 60 hours and their fluxes were calculated together, so we reported six typhoons but only five fluxes.