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An Advanced PMF Model Based on Degradation Process for Pollutant Apportionment in Coastal Areas

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Abstract: With increasing stress posed to the marine ecosystem and coastal communities, prevention and control of coastal pollution becomes urgent and important, in which the identification of pollution sources is essential. Currently, the pollutant source apportionment in coastal areas is mainly based on receptor models, such as the positive matrix factorization (PMF) model. Nevertheless, these models still lack consideration of the changes of pollutant behaviors (e.g., the degradation of pollutants) which cause the differences in pollutant compositions. Subsequently, the source apportionment via receptor models only based on the monitoring data may not be consistent with the one in pollution sources. To fill this gap, a pollutant degradation model was firstly developed in this study. Accordingly, the degradation model was inversed to estimate the pollutant concentrations at their emitting sources, based on the monitoring concentration in the coastal area. Finally, the estimated concentrations were fed to the PMF model for pollutant source apportionment, advancing the PMF model with degradation process. To demonstrate the feasibility and accuracy of the developed model, a case study of source appointment was carried out based on the polycyclic aromatic hydrocarbons (PAHs) in the sediments of the Pearl River Estuary. The results indicated the same types of emission source identified by the original and advanced PMF models, which were oil spill, biomass and coal combustion, and traffic emission. Nevertheless, the contributions of sources were significantly varied between the two models. According to the analyses based on emission inventory, the offsets of the results from the original PMF model were −55.4%, 22.7%, and 42.2% for the emission sources of oil spill, biomass and coal combustion, and traffic emission, respectively. Comparatively, the offsets for the advanced PMF model narrowed down to −27.5%, 18.4%, and −4.4%. Therefore, the advanced PMF model is able to provide satisfactory source apportionment for organic pollutants in coastal areas, and thus further provide a scientific basis for marine pollution prevention and control.

Keywords: coastal pollution; source apportionment; receptor model; PAHs

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1. Introduction

With the rapid development of economy, urbanization and industrialization have also significantly increased. These processes have greatly improved the living quality but have also introduced various environmental pollution problems. As the most ideal sink of pollutants, the ocean is gradually damaged due to the increasing types and discharge amounts of pollutants as well as their accumulation in the marine system. This impact is of significance in coastal areas which are directly adjacent to the areas with high-intensity human activities.

Consequently, prevention and control of coastal pollution become urgent and important, and the identification of pollution sources is essential [1]. However, due to the diversity of pollution sources and the complexity of environmental conditions [2–4], it is difficult to directly identify the pollution sources according to the pollutants detected in the coastal area. Currently, several numerical models, such as the inversion of dispersion models [5,6], as well as the receptor models [7,8], have been developed to facilitate the pollutant sources apportionment. Among these models, the receptor models are the group of models that are most widely applied for the pollutant source apportionment in coastal environments [4].

The mainly used receptor models include the chemical mass balance (CMB) model, factor analysis (FA), factor analysis with nonnegative constraints (FA-NNC), absolute principal component score with multiple linear regression (APCS-MLR), principal component analysis with multiple linear regression (PCA-MLR), and positive matrix factorization (PMF) [9–13]. In recent years, the widely used models include the PCA, PCA-MLR, and PMF. Although these models were originally developed for the source apportionment of pollutants in atmospheric environments [4], their applications in marine environments, especially coastal environments, have been increasing in recent years. For example, Jafarabadi et al. (2020) analyzed the source apportionment of poly brominated diphenyl ethers (PBDEs) in the Persian Gulf based on PCA, which indicated that the PBDEs in the water column and sediment of the Persian Gulf were from the same sources [14]. In addition, Odabasi et al. (2017) utilized the PCA model to conduct the source apportionment of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) in the coastal area of an industrial zone in Turkey, indicating two sources of the pollutants: steel industry and traffic emissions [15]. Couple studies were also conducted to analyze the source apportionment of PAHs in the coastal areas of Canada, India, and Korea, respectively [16–18]. These studies indicated that the possible sources of PAHs were traffic emission, coking, biomass burning, and coal burning. Furthermore, Wu et al. (2019) compared the efficiencies of PCA and PMF in the source apportionment of PAHs in the coastal area of Bohai, China [19]. The research indicated a better performance of PMF than PCA in the source apportionment of pollutants in coastal areas.

Nevertheless, all the current receptor models proceed the source apportionment only based on the concentration of pollutants sampled in the coastal waters and/or sediments instead of the concentration or mass loading of them at the emission sources. However, along with the path of pollutants transmitted from emission sources to the coastal water/sediment, a series of transport and fate processes (e.g., degradation, adsorption–desorption, sedimentation, etc.) occur and affect the composition of pollutants, especially for organic pollutants [20,21]. Subsequently, the apportionment of pollutants at the sampling locations would be different from that at the location of emission sources. Such difference would be enlarged for the pollutants in coastal areas, due to longer distance of pollutant transport and interval of sampling activities.

To fill this gap, this research aims at the advancement of the receptor model (i.e., the PMF model) with the consideration of the fate processes (i.e., degradation) of pollutants. Correspondingly, the applicability and accuracy of the original and proposed model will be analyzed based on a case study of pollutant source apportionment in a coastal area. The proposed model is expected to provide satisfactory applicability and accuracy in pollutant source apportionment in coastal areas.

2. Methodology

2.1. Degradation Model and Its Inversion

The degraded portions of different degradable pollutants (e.g., most of the organic pollutants) will be different along with time due to the differences of their degradation rates. The difference of degradation rates for different pollutants can vary up to several orders of magnitudes. Such differences will cause significant variation of pollutant compositions from emission sources to the coastal area. In order to reflect the compositions of pollutants at the emission sources based on their concentration at the sampling locations in the coastal area, a degradation model with inversion shall be needed.

Current research indicates that the degradation of an organic pollutant usually follows the pseudo-first-order kinetic model, as follows [22,23]:

$$\frac{d[c]}{dt} = -k[c] \tag{1}$$

where t is the time span of degradation (T), c is the concentration of pollutant ($\mathrm{M{\cdot}L^{-3}}$) at time t, and k is the degradation rate constant ($\mathrm{T^{-1}}$). Usually, the pollutant source apportionment based on receptor models considers that the discharge of the pollutant is continuous and stable. According to this assumption, Equation (1) can be revised as follows:

$$\frac{d[c]}{dt} = -k[c] + D \tag{2}$$

where D reflects the change of concentration ($\mathrm{M{\cdot}L^{-3}}$) in a coastal area due to the discharge from emission sources. Based on an assumption that the volume of the water column is unchanged along with time, D is linearly correlated with the mass load (flux) of the pollutant at emission sources. Accordingly, the ordinary solution for Equation (2) is as follows:

$$c = Ae^{-kt} + \frac{D}{k} \tag{3}$$

where A is an integral constant. The determination of constant A relies on the change of concentration (D) caused by the emission during the study period, as well as the background concentration at the starting point of the study period. When only one set of monitoring data is obtained for the area, and the background concentration is undetected, difficulty exists in the determination of constant A. Nevertheless, if the simulation period (Δt) is the same as the time period of the water exchange or sediment exchange cycle of the target area, the effect from the background concentration can be ignored. Correspondingly, Equation (3) can be revised as follows:

$$c = -\frac{D}{k}e^{-kt} + \frac{D}{k} \tag{4}$$

Assuming the simulation period is Δt and the concentration of a pollutant at certain sampling location is c_0 ($\mathrm{M{\cdot}L^{-3}}$), Equation (4) can be further revised as follows:

$$D = \frac{c_0 k}{1 - e^{-k\Delta t}} \tag{5}$$

where c_0 is the concentration of the pollutant based on the sampling and analyses activities.

The parameter D represents a nominal concentration caused by the continuous emission of certain pollutant in every sampling location that can be estimated. The nominal concentration is what concentration a degradable pollutant would cause in a sampling location if it is assumed to be non-degradable. This concentration is linearly related to the mass load (flux) of this pollutant at the emission source.

2.2. Advance of the PMF Receptor Model Based on Degradation Process

Based on Equation (5), the nominal concentration for each pollution in each sampling location can be calculated. These concentrations will be fed to the reception model for pollutant source apportionment. The target receptor model used in this study is the PMF model.

The PMF model was firstly introduced by Paatero and Tapper in the 1990s [24–26]. After being leased and suggested by the U.S. Environmental Protection Agency (US EPA), the PMF model has been widely used. The basic algorithm of PFM is as follows:

$$X_{ij} = \sum_{k=1}^{p} (G_{ik}F_{kj} + E_{ij}) \tag{6}$$

where X_{ij} is the concentration of ith composition (pollutant) in the sample taken in the jth location, G_{ik} is the concentration of ith composition (pollutant) at the kth emission source, F_{kj} is the contribution of the kth emission source in the sample taken in the jth location, and E_{ij} is the residual term.

Based on the nominal concentrations, a concentration matrix X' can be developed with a dimension of $n \times m$, where n is the number of sampling locations, and m is the type of pollutants. Based on the decomposition of matrix X', two matrixes, G and F, can be generated. G is the matrix of contributions from emission sources, with a dimension of $n \times p$, where p is the number of emission sources. F is the matrix of emission source profile. Correspondingly, a minimize model is introduced to minimize the difference (Q) between X' and G × F, as follows:

$$\mathrm{min}Q = \sum_{i=1}^{n}\sum_{j=1}^{m}\left[\frac{X'_{ij} - \sum_{k=1}^{p} G_{ik}F_{kj}}{Unc_{ij}}\right]^2 \tag{7}$$

where Unc_{ij} is the matrix representing the uncertainty degree of the data. In the case that multiple samples are taken from a certain location, the standard deviation of the measured concentrations for these samples can be used to represent the *Unc*. Otherwise, when the detected concentration is lower than the method detection limit (MDL), the *Unc* is calculated as follows:

$$Unc = \frac{5}{6} \times MDL \tag{8}$$

When the detected concentration is higher than the MDL, the *Unc* is calculated as follows:

$$Unc_{ij} = \sqrt{\left(Error\ Fraction \times X'_{ij}\right)^2 + (0.5 \times MDL)^2} \tag{9}$$

where *Error Fraction* is the relative standard deviation (RSD) of the concentrations for the corresponding pollutant.

2.3. Analysis of Modeling Results Based on Indirect Emission Inventory

It is difficult to directly compare the accuracy of source apportionment results from different receptor models, because the actual contribution of certain emission sources to the receptor (e.g., the water column of a coastal area) is usually unclear. The emission inventory in the surrounding area can be a potential indicator for the comparison. The emission inventory is a method that comprehensively investigates the relation between the mass load (flux) of certain pollutants and different types of emission sources in a certain period (usually an annual period) with quantification [27]. The emission inventory has been well developed for the source apportionment of atmospheric pollutants. However, emission inventory for water pollution, especially marine pollution, is still insufficient [28]. Thus, this study utilized the emission factor to develop the emission inventory, as follows:

$$EI = EA_{ij} \times EF_{ij} \tag{10}$$

where *EI* is the mass load or flux of a pollutant, EA_{ij} is the human activity level corresponding to the jth composition (pollutant) in the ith emission source, and EF_{ij} is the emission factor of the jth composition (pollutant) in the ith emission source. The human activity level is the human activities that can affect the emission of the target pollutant, such as the flux from industrial discharge, the amount of fuel burning, the usage of pesticides, etc. [20,29,30]. On the other hand, the emission factor is the emission rate of the pollutant from a certain type of human activity [29]. By comparing the modeling results and the *EI* value, the accuracy of the model can be analyzed.

3. Case Study

In order to demonstrate the feasibility and accuracy of the degradation process-advanced PMF model, a case study of source appointment was conducted based on the polycyclic aromatic hydrocarbons (PAHs) in the sediments of the Pearl River Estuary, China. For comparison, a case study based on the original PMF model was also conducted with the same datasets and settings.

3.1. The Study Area and Pollutants

The study area was the Pearl River Estuary (PRE) in southern China, which is the most important estuary in the South China Sea (Figure 1). The PRE is also one of the most important fishing grounds in China, with abundant fishery resources and high biodiversity [31]. On the other hand, this region is also suffering from high stress of human activities. Various types of pollutants have been massively and continuously discharged into the Pearl River and surrounding atmosphere, eventually accumulating in the PRE [32,33]. Subsequently, the water quality in the PRE remains at a low level [34].

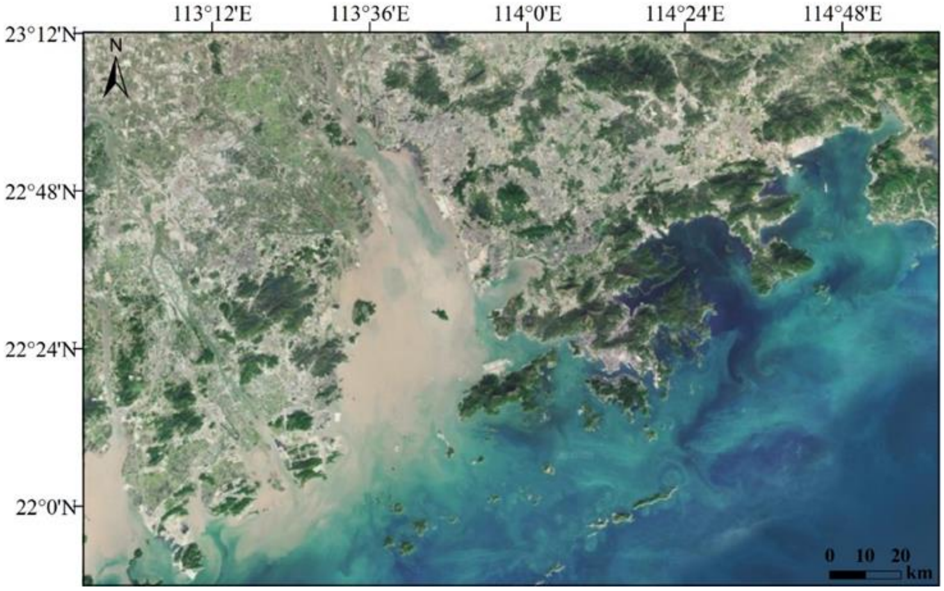

Figure 1. Map of the Pearl River Estuary.

There are many organic pollutants that have been detected in the PRE, in which PAHs are an important group of pollutants, attracting more and more attention. Corresponding studies indicated that the PAHs remained at high concentrations and were detected in edible fishes in the PRE [35–37]. Therefore, the pollution prevention and control of PAHs are urgently required for this area, and source apportionment is one of the key processes.

3.2. Data Sources of the PAHs Concentrations

This research focuses on the 16 PAHs which were designated as high-priority pollutants by the US EPA, including naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyren (BaP), dibenz[a,h]anthracene (DahA), indeno [1,2,3-cd]pyrene (IcdP), and benzo[g, h, i]pyrene (BghiP).

The data sources used in this study were from Yuan et al. (2015) [38] and Zhang et al. (2015) [39], representing the monitoring data in 2011 and 2012, respectively. The corresponding concentrations for the 16 PAHs are listed in Tables S1 and S2. It is worth noting that the sampling locations from Yuan et al. (2015) included the regions of the PRE (45 sampling points, P1–P45), the northern South China Sea (3 sampling points, S1–S3), and Daya Bay (17 sampling points, D1–D17). Since the sampling locations in the northern South China

Sea and the Daya Bay were far from the PRE region, the data from these locations were omitted from this study. In addition, concentrations of the 16 PAHs in sampling location A1 from Zhang et al. (2015) were significantly higher than those from the other locations. The location of A1 is in the upstream of the Pearl River and far away from the other sampling locations. This location is also highly affected by the human activities, compared to the other sampling locations. Thus, the data from this sampling location were also omitted from this case study. The compositions of the 16 PAHs according to the monitoring data from 2011 and 2012 are illustrated in Figure 2.

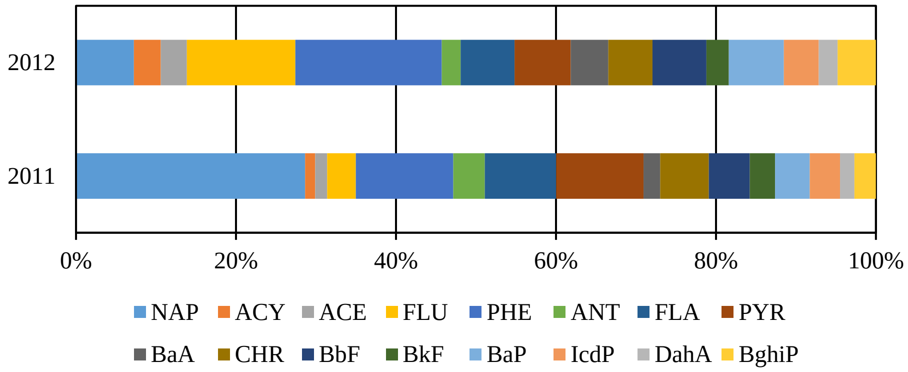

Figure 2. The compositions of PAHs from the PRE in 2011 and 2012.

3.3. Model Settings

The original PMF only requires the concentration of the 16 PAHs for the source apportionment. Comparatively, the advanced PMF model requires additional data for the simulation of PAHs degradation. Unfortunately, due to insufficient research on the degradation of PAHs in sediments, the corresponding degradation rates constants (k) were incomplete recently. As an alternative, the degradation rates for the 16 PAHs in soil were used in this study, because the soil environment is relatively close to the sediment environment, compared to water and atmospheric environments [40]. Although the values of k were different between the soil and sediment environments, their trends might be similar, which was sufficient for the estimation for the change of pollutant compositions. The corresponding degradation rates for the 16 PAHs are listed in Table S3.

The period for the simulation was set to one year. This time span is sufficient for the simulation of the advanced model since the annual sedimentation depth of sediments in the PRE (2 $\text{cm}\cdot\text{a}^{-1}$) was larger than the sampling depth (0–2 cm) [41]. In addition, the time span of one year was satisfactory for the generation of emission inventory based on the annual census of the data.

When the number of emission sources was set to three, the best regressions between the prediction and the monitoring data were observed for both the original and advanced PMF models. Thus, three PMF factors (emission sources) were considered in the case study.

3.4. Results and Discussion

The correlations between modeling results and the monitoring data are listed in Tables S4–S7. When the types of emission sources were set to three, both the original and advanced PMFs could provide satisfactory source apportionment for the 16 PAHs in 2011 and 2012. Only one exception was observed, for BghiP in 2012. The correlation coefficients for BghiP were significantly lower than the other PAHs for both models. This was probably due to some unknown inputs of BghiP to one or more sampling locations, affecting the accuracy of source apportionment for BghiP. Thus, BghiP is omitted in the discussion.

The source profiles based on the original and advanced PMF model are shown in Figures 3 and 4. Factors 1 to 3 represent different types of emissions which still remained unknown in the raw outputs and required further analyses. In Factor 1, the proportion of NAP was dominant. According to the literature, NAP was mainly from petroleum hydrocarbon discharges such as leakage from pipelines, oily wastewater discharge from refinery, and oil spill events from oil production and transportation [42–44]. Therefore, Factor 1 was identified as the emission source of oil spill. In Factor 2, ANT, FLU, and PHE appeared in relatively high proportions. Usually, ANT and PHE were indicators for combustion of biomass or coal [45], while the FLU and PHE were indicators for coal combustion [46]. Correspondingly, Factor 2 was defined as the emission source of biomass and coal combustions. Furthermore, high-molecular-weight (HMW) PAHs (usually with four or more aromatic rings), such as CHR, BbF, BkF, BaP, IcdP, and DahA, appeared in high proportions in both 2011 and 2012. Recent research indicates that the IcdP is mainly released from traffic emission [47]. In addition, BbF and BaP were indicators for the combustion of diesel (e.g., marine diesel oil for tanker or vessel). Thus, Factor 3 was identified as the emission source of traffic emission.

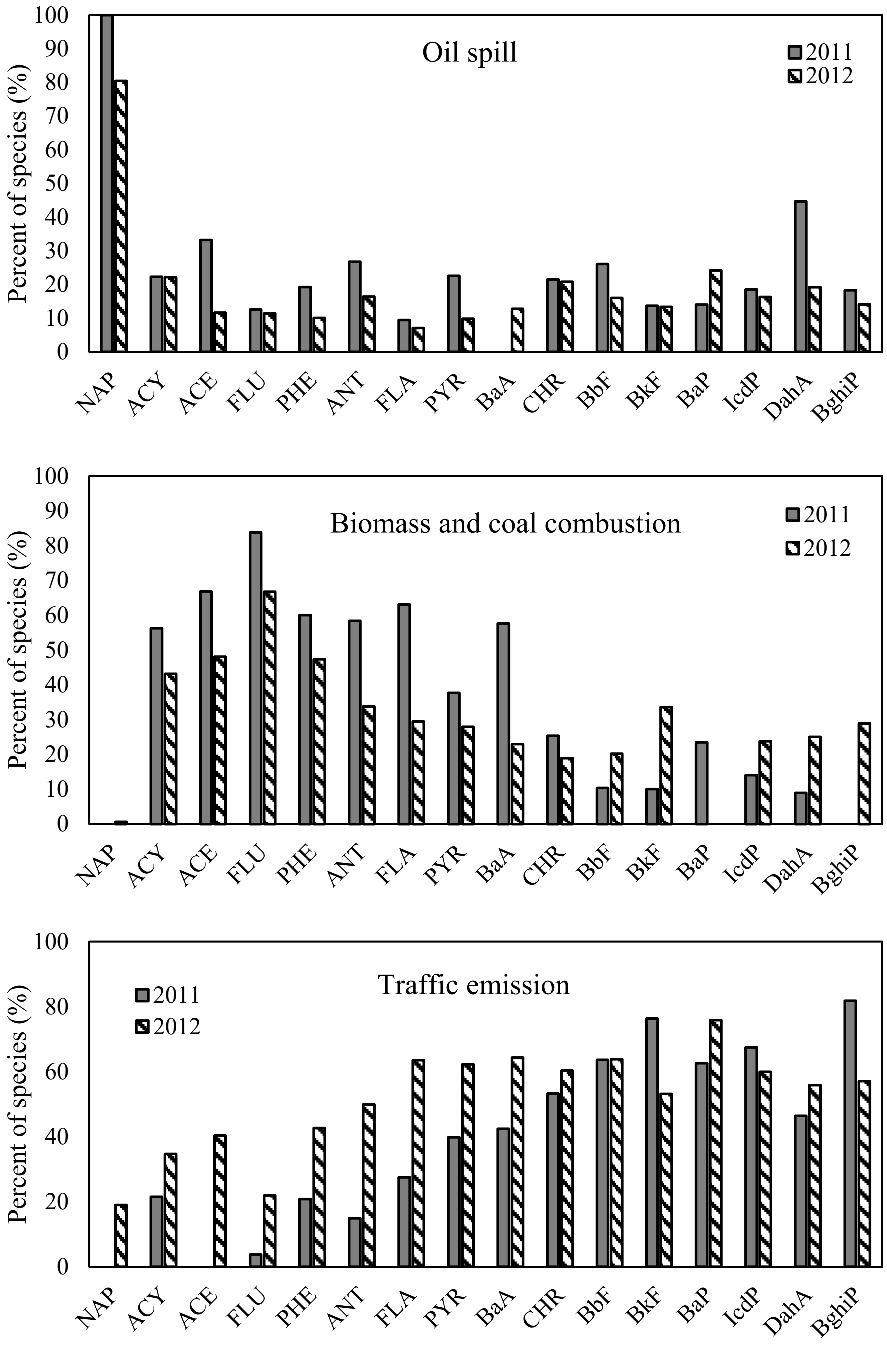

Figure 3. PAHs source profiles in 2011 and 2012 based on original PMF modeling result.

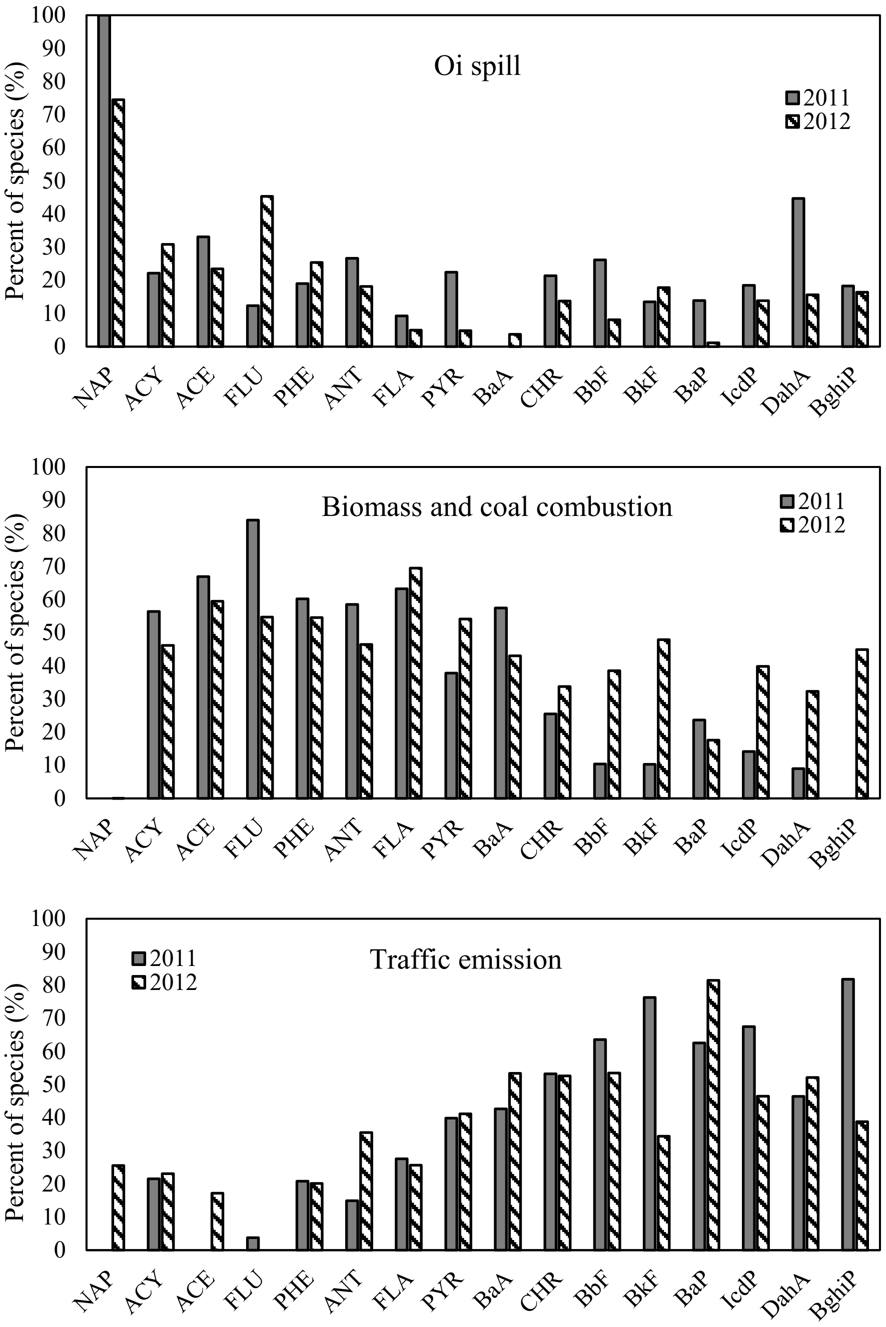

Figure 4. PAHs source profiles in 2011 and 2012 based on advanced PMF modeling result.

After the sources were identified, their contributions were further analyzed. Based on the original PMF model, the contributions for the sources of oil spill, biomass and coal combustion, and traffic emission were 39.28%, 28.87%, and 31.85% in 2011, and 16.70%, 35.72%, and 47.58% in 2012. The corresponding changes of contributions were −55.7%, 23.8%, and 49.4% from 2011 to 2012. According to the social–economic development in the area surrounding the PRE from 2011 and 2012, the activities relating to oil spill (e.g., oil refinery and transportation, marine traffic) were prosperous. Thus, it was difficult to interoperate the significant decrease of oil spill contribution. In addition, although the number of automobiles were high in the area, it was also difficult to explain such a high increasing percentage of the traffic emission.

The advanced PMF identified the same emission sources as the original one. Nevertheless, the corresponding contributions were different. Based on the advanced PMF model, the contributions for the sources of oil spill, biomass and coal combustion, and traffic emission were 25.25%, 43.57%, and 31.18% in 2011, and 17.32%, 51.61%, and 31.07% in 2012. The corresponding changes of contributions were −22.2%, 18.4%, and −0.4%. Compared to the original PMF model, the results from the advanced PMF model appeared smoother annual changes of the contribution from different emission sources, which would be more reasonable as they were more in line with the social–economic development of the area. However, the more detailed model accuracies could not be quantified by this comparison.

In order to analyze in-depth the accuracy of the original and advanced PMF models, the indirect emission inventory method was applied. Currently, there is still a lack of the emission inventory for PAHs in marine sediments. Comparatively, the emission inventory for PAHs in the atmosphere was well developed. Furthermore, it was indicated that the PAHs in marine water columns and sediments were mainly from the deposition of atmospheric PAHs [48]. Thus, the emission inventory for PAHs in marine sediments could be developed based on the one in the atmosphere. The corresponding inventories are listed in Table 1.

Table 1. Emission inventory for PAHs.

Emission Sources	**Oil Spill**	**Biomass and Coal Combustion**	**Traffic Emission**
Emission inventory	Oil refinery Oil spill or oily water from tanker or vessel * Leakage or spill from pipeline *	Coal for power plants or industry Coal for community Coal for coking Straw burning Wood burning Forest fire	Gasoline combustion Diesel combustion Combustion of other fuel oils

* Usually is not considered in atmospheric environments but is important for marine environment.

Based on the emission inventory, corresponding human activities were determined and quantified based on the annual census and the literature in the area. In this study, the data reflecting the human activities in the PRE area were based on the annual census of Guangdong Province, China in 2011 and 2012 [49,50]. The corresponding datasets are listed in Table 2.

Table 2. PAHs related to human activities in 2011 and 2012.

Source of PAHs		**Year**		**Change from 2011 to 2012 (%)**
		2011	**2012**	
Oil spill	Crude consumption (ton/day)	462	437	94.59
	Cargo throughput (10^6 ton/year)	133,704	140,776	105.29
	Total length of pipeline (km)	6436.91	6448.01	100.17
Biomass and coal combustion	Consumption of coal and coke (ton/day)	169,244	165,864	98.00
	Rice production (10^3 ton/year)	10,969.0	11,265.7	102.70
Traffic emission	Gasoline consumption (ton/day)	32,995	34,379	104.19
	Diesel consumption (ton/day)	40,812	42,122	103.21
	Consumption of other fuel oils (ton/day)	10,634	8427	79.24

According to Table 2, only the crude consumption decreased, but the others increased, for the emission source of oil spill. However, both the original and advanced PMF models indicated decreased contributions of oil spill. In addition, no oil spill event was reported from 2009 to 2013 in the PRE and its surrounding areas. Thus, it was assumed that the PAHs from the emission source of oil spill were mainly from the regular oily wastewater discharge from oil refineries. Accordingly, the change of human activities relating to oil spill was 94.59% from 2011 to 2012. The human activities relating to biomass and coal combustion were very close in 2011 and 2012, and thus the ratio was set to 100%. For the emission source of traffic emission, the major contribution would be from the combustion of gasoline and diesel. The other fuel oils were mainly marine diesel oils for tankers and vessels which would leave the PRE shortly after the oil tanks were filled. Since the ratio of gasoline and diesel consumptions was close, the one for the gasoline (104.19%) was selected to present the change of traffic emission from 2011 to 2012.

According to the ratios of PAH-related human activities, as well as the contribution of each emission source in 2011 based on the original and advanced PMF model, the corresponding contribution in 2012 was estimated. This contribution was defined as the contribution estimated by human activities (CEHA). The contributions based on the monitoring data in 2011 and 2012, as well as the CEHA, were illustrated in Figures 5 and 6. The contribution differences between CEHA and the 2012 data based on the original PMF model were −55.4%, 22.7%, and 42.2% for the emission sources of oil spill, biomass and coal combustion, and traffic emission, respectively. Comparatively, the differences between CEHA and the 2012 data based on the advanced PMF model were −27.5%, 18.4%, and −4.4%. According to the comparison, significant gaps still existed between the results from the original PMF model and the CEHA for the emission sources of oil spill and traffic emission. Comparatively, the difference between the results from the advanced PMF model and the CEHA were acceptable, indicating the advantage of the advanced model.

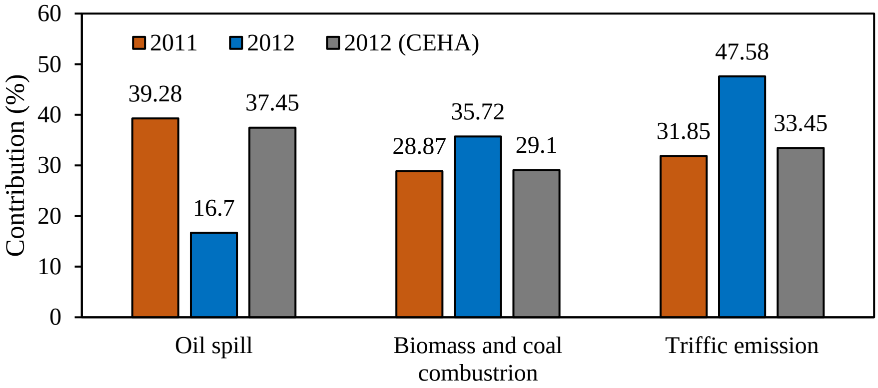

Figure 5. Source contributions based on the original PMF model.

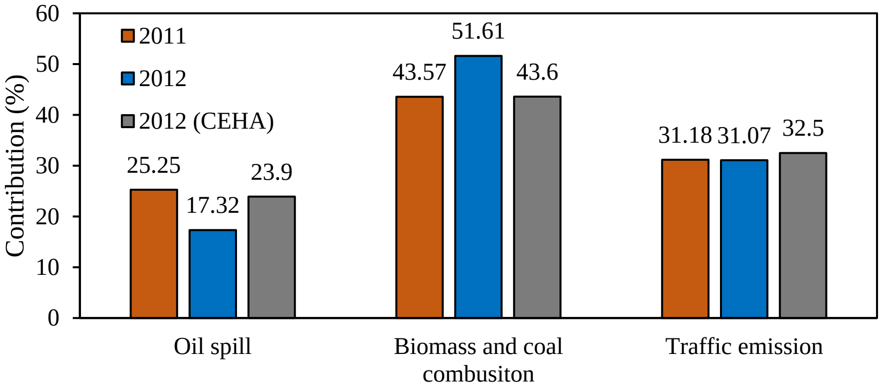

Figure 6. Source contributions based on the advanced PMF model.

4. Conclusions

In this study, one of the most widely used models for pollutant source apportionment, the positive matrix factorization (PMF) model, was advanced with the consideration of pollutant degradation. Firstly, the degradation of pollutant was simulated based on the pseudo-first-order kinetic model. Accordingly, the degradation model was inversed to estimate the nominal concentration of the pollutant, reflecting the mass load (flux) of this pollutant at emission sources. The nominal concentrations were fed to the reception model for pollutant source apportionment, instead of the raw concentrations from monitoring.

Furthermore, an indirect emission inventory method was developed to analyze the accuracy of the pollutant source apportionment.

To demonstrate the applicability and accuracy of the advanced PMF model, a case study was carried out focusing on the source apportionment for PAHs in the sediment of the Pearl River Estuary (PRE), China, in 2011 and 2012. For comparison, a case study was also conducted based on the original PMF model with identical inputs and model settings. Both the original and the advanced models identified three types of emission sources for the PAHs in PRE: oil spill, biomass and coal combustion, and traffic emission with varied contribution. In 2011, the original PMF model indicated the source contributions of oil spill, biomass and coal combustion, and transportation emission of 39.28%, 28.87%, and 31.85%, respectively. Comparatively, the advanced model indicated the source contributions of 25.25%, 43.57%, and 31.18%. In 2012, the original PMF model indicated the corresponding contributions of 16.70%, 35.72%, and 47.58%, while the advanced model indicated 17.32%, 51.61%, and 31.07%. Compared to the original PMF model, the results from the advanced model were more consistent with the social–economic development of the area surrounding PRE. Based on the analyses via indirect emission inventory, the offsets of the results from the original PMF model were −55.4%, 22.7%, and 42.2% for the emission sources of oil spill, biomass and coal combustion, and traffic emission, respectively. Comparatively, the offsets for the advanced PMF model narrowed down to −27.5%, 18.4%, and −4.4%, indicating the advantage of the advanced model.

In general, the advanced PMF model can provide satisfactory source apportionment for organic pollutants in coastal areas. In future study, the other pollutant transport and fate processes (e.g., adsorption–desorption, sedimentation, air–sea exchange) will be further considered. In addition, the change of pollutant flux and discharge period will also be considered in the advanced model to better reflect the real-world conditions. Furthermore, the datasets of 2011 and 2012 PAHs concentration were used to demonstrate the feasibility and accuracy of the advanced PMF model; more recent datasets will be continuously collected to further test and advance the model.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14111823/s1: Table S1: Concentration of 16PAHs ($\mu g \cdot g^{-1}$) in sediments from the Pearl River Estuary, 2011; Table S2: Concentration of 16PAHs ($\mu g \cdot g^{-1}$) in sediments from the Pearl River Estuary, 2012; Table S3: Degradation rates of PAHs; Table S4: Correlations between modelling results and monitoring data in 2011 based on the original PMF model; Table S5: Correlations between modelling results and monitoring data in 2012 based on the original PMF mode; Table S6: Correlations between modelling results and monitoring data in 2011 based on the advanced PMF model; Table S7: Correlations between modelling results and monitoring data in 2012 based on the advanced PMF model. References [51–55] are cited in the supplementary materials.

Author Contributions: P.L.: conceptualization, methodology, investigation, supervision, writing—original draft; X.C.: data curation, investigation, validation, formal analysis; H.N.: investigation, resources, writing—review and editing; Z.L.: writing—review and editing, visualization; Z.Z.: writing—review and editing; G.L.: project administration, funding acquisition; K.Y.: data curation, writing—review and editing, project administration, data acquisition. All authors have read and agreed to the published version of the manuscript.

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"Zhang, J.; Wang, Y.; Cheng, H.; Jiang, Z.; Sun, C.; Wu, M. Distribution and sources of the polycyclic aromatic hydrocarbons in the sediments of the Pearl River estuary, China. *Ecotoxicology*. **2015**, 24, 1643–1649" [39].

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