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Source identification and characterization of atmospheric polycyclic aromatic hydrocarbons along the southwestern coastal area of Taiwan – with a GMDH approach

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ABSTRACT

Air samples of polycyclic aromatic hydrocarbons (PAHs) were collected from May 2008 to April 2009 in the Kaohsiung coastal area of Taiwan to establish a dataset. Sample analysis suggested that PAH composition (dominated by 3-ring PAHs) and seasonal patterns (high concentration in winter and low concentration in summer) are nearly identical to those previously reported (Lai et al., 2011), except for a case of road construction during the sample period. The predominant sources of PAHs were identified by isomer ratio, HCA and PCA analyses as vehicle emissions and coal/wood combustion. According to the results of parameters selection via the Group Method of Data Handling (GMDH), the variations in gaseous PAHs and particulate PAHs were related mainly to meteorological conditions and to routine monitoring of air pollutant concentrations, respectively. A comparison of model prediction accuracy between particulate and gaseous PAHs suggests better prediction for particulate PAHs than gaseous PAHs, due to dramatic variation in meteorological conditions which results in higher prediction uncertainty for gaseous PAHs. Model predictions of PAH concentrations showed satisfactory agreement with measured data, except for specific incidents, such as joss paper burning events. The results of this study suggest that the GMDH model may be applied to PAH concentration prediction for the study area and may be applicable for other countries based on routine monitoring of air pollutant concentrations and meteorological conditions.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic compounds found ubiquitously in the environment. They are well known for their chemical characteristics and for their harmful effects on human health. PAHs are generated mainly from incomplete combustion and pyrolysis processes resulting from anthropogenic activities, including wood combustion (Baek et al., 1991; Benner et al., 1995), fuel combustion in vehicles, and residential heating systems (Benner et al., 1989; Mastral and Callen, 2000). Natural sources (e.g., forest fires and volcanoes) also contribute to environmental PAH burden. PAHs are hydrophobic organic compounds (HOCs) and can exist in both the gaseous and particulate phases in the atmosphere (Park et al., 2002). Some PAHs, in particular the high molecular weight PAHs, have been identified as health hazards due to their potential carcinogenicity and mutagenicity to humans (Grimmer, 1983; IARC, 1984; WHO, 1987). Their high stability in the environment and their adverse effects on human health have prompted extensive study of their sources and environmental fate in recent decades.

Our previous study documented the seasonal variation of PAHs in the Kaohsiung coastal area (Lai et al., 2011). The findings suggested that land-sea circulation and monsoon activities played important roles in determining diurnal and seasonal variation of PAHs, respectively. In addition to the factors identified above, other meteorological factors (e.g., wind direction, temperature, and rainfall) also may affect the seasonal variation and distribution of PAHs in the Kaohsiung coastal area. Understanding the other potential influencing factors underlying PAH pollution is useful for determining strategies for air quality control in the study area. In addition, the current state of the art experimental analysis of PAHs involves extensive labor, and prolonged sampling

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and analysis times. To mitigate the disadvantages of routine experimental analysis, a modeling approach (e.g., air pollution models) may be useful in regulating PAH pollution in the study area.

Air pollution models can be used to explain the causal relationship between emission sources, atmospheric concentration, and environmental conditions (e.g., meteorological conditions) (Daly and Zannetti, 2007). They could also play an indispensable role in regulatory applications, because of their capability to predict pollutant concentrations for environmental impact assessments (Hurley et al., 2001). Over the past several decades, a number of air pollution models have been developed based on functional design and numerical parameters (Daly and Zannetti, 2007). These models can provide regulatory information efficiently; however, the need for a variety of input parameters and the enormous quantity of pollution data make application of these models difficult.

In this study, the Group Method of Data Handling (GMDH) approach was utilized as an alternative air pollution model due to data limitations. GMDH, based on the concept of the Rosenblatt Perceptron, was introduced by A.G. Ivakhnenko in 1966 (Farlow, 1981; Madala and Ivakhnenko, 1994). This algorithm is able to establish an optimal, multilayered neural network model for sorting out the problem of identifying causal relations between multiple factors and an object of complex systems (e.g., economic, ecological, and environmental systems) using a heuristic self-organization approach with numerical values for input variables (Ivakhnenko, 1978; Farlow, 1981; Yoshimura et al., 1982; Madala and Ivakhnenko, 1994). GMDH has been widely applied in diverse fields, including ecological systems analysis and prediction, environmental systems, and medical diagnostics, among others. For instance, Zhu et al. (2012) studied the relation between air pollution and respiratory disease using both association rules and GMDH. Abdel-Aal (2007) developed a predictive model of mercury speciation in combustion flue gases using GMDH. Reddy and Pachepsky (2000) applied GMDH to estimate crop yields based on climatic variable, including CO_2 level, total solar radiation, temperature, and rainfall. These studies showed that GMDH is characterized by simplified and automated model synthesis, automatic selection of significant inputs, and more transparent input–output model relationships than other approaches.

GMDH is a data-oriented modeling approach that selects model structures using the implicit information embedded in data to avoid preconceived conditions on the part of researchers. In addition, GMDH can be effective in problems with smaller data samples or with short-term periodic prediction (Farlow, 1984; Madala and Ivakhnenko, 1994). Given the data limitations of the present study, applying GMDH could be beneficial, since the air pollution data is limited and seasonal variation in the pollution pattern is expected.

This study is a sequel to our previous investigation (Lai et al., 2011). The aims of the present study comprised two parts: the first was to construct a second-year dataset by analyzing both gaseous and particulate PAH concentrations; the temporal variation of PAH concentration and pollution sources were investigated as well. The second part was to use the numerical approach of the GMDH to study the interrelationship between PAH pollution and factors such as air pollutants (ozone, SO_2, NO_x, NO_2, NO, PM_{10}, and $PM_{2.5}$) and meteorological conditions (temperature, pressure, humidity, wind speed, wind direction, three-day rainfall accumulation and intensity, and five-day rainfall accumulation and intensity), then to develop an efficient approach for prediction of PAH concentrations in the Kaohsiung coastal area.

2. Material and methods

2.1. Sampling and analysis

Air samples were collected at the same sampling location (22°37′N, 120°15′E, Fig. 1) used in the previous study (Lai et al., 2011). Selection of the sampling site, which is in the neighborhood of Kaohsiung Harbor, took into account the representative PAH transport pattern in the southwestern coastal area of Taiwan. Samples were taken at least once per month over a 12-month period between May 2008 and April 2009.

Air sampling processes, equipment pre-treatment procedures, and sample extraction, preparation, and analysis procedures were adapted from Lai et al. (2011). Briefly, the particulate and gaseous PAHs were collected on quartz fiber (QF) and polyurethane foam filters (PUF) via a high volume sampler. Air samples were retrieved every 24 h during each sampling event at a flow-rate of 13.5 $m^3\ h^{-1}$. During each sampling event, hourly meteorological data, including air temperature, precipitation, average wind speed, and prevailing wind direction were collected from the Qianzhen station of the Central Weather Bureau.

The QF and PUF samples were extracted with dichloromethane and petroleum ether, respectively. The extracts were concentrated to 5 mL in a rotary evaporator, then fractionated using aluminum oxide and anhydrous sodium sulfate (1 cm), and purified by petroleum ether. The resulting extracts were concentrated to 0.5 mL by evaporation under a nitrogen stream for GC–MS analysis. A capillary gas chromatograph (Agilent 6890N) and a mass spectrometer (Agilent 5973N), operating under the selected ion monitoring mode, were used to identify and quantify PAHs from samples. Prior to analysis, a mixture of perdeuterated PAHs [acenaphthene-d_{10}, phenanthrene-d_{10}, benzo(a)anthracene-d_{10}, and benzo(a)pyrene-d_{12}, and benzo[g,h,i]perylene-d_{12}] was added as an internal standard. Each PAH was identified by retention time relative to the internal standards and quantified by comparing the integrated area of the molecular ion chromatogram to those of the standards.

In this study, four perdeuterated PAHs (naphthalene-d_8, fluorene-d_{10}, fluoranthene-d_{10}, and perylene-d_{12}) were added to each sample prior to extraction as surrogates for determination of the efficiency of extraction and analysis. The mean recoveries of PUF samples were 61.2 ± 8.6%, 87.6 ± 7.3%, 94.7 ± 16.2%, and 90.0 ± 7.7%

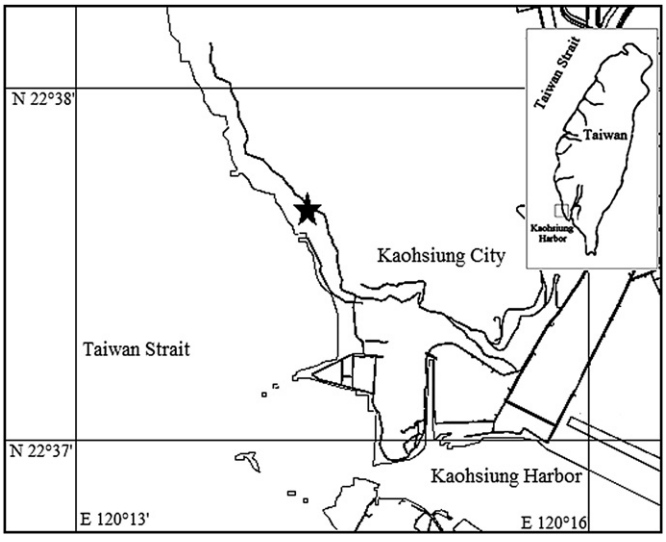

Fig. 1. Map of sampling site, southwest Taiwan. Star symbol indicates the location of the sampling site.